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Separation of Plutonium from Irradiated Fuels and Targets

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Chapter 28

Separation of Plutonium from Irradiated Fuels and Targets

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Separation of Plutonium from Irradiated Fuels And Targets

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Chapter 28

I. INTRODUCTION

The production of electricity by nuclear fission is, at present, nearly 366-gigawatt electric (GW_e), generated from 438 operating nuclear reactors. Unlike fossil fuel ash, with limited residual available energy content and negligible heat content, the spent nuclear fuel from power production reactors contains moderate amounts of transuranium (TRU) actinides and fission products in addition to the still slightly enriched uranium. Originally nuclear technology was developed to chemically separate and recover fissionable plutonium from irradiated nuclear fuel for military purposes. Military plutonium separations had essentially ceased by the mid-1990s. Reprocessing, however, can serve multiple purposes and the relative importance has changed over time. In the 1960's the vision of the introduction of plutonium-fueled fast-neutron breeder reactors drove the civilian separation of plutonium. More recently, reprocessing has been regarded as a means to facilitate the disposal of high-level nuclear waste and thus requires development of radically different technical approaches. In the last decade or so, principal reason for reprocessing has shifted to spent power reactor fuel being reprocessed 1) so that unused uranium and plutonium being recycled reduce the volume, gaining some 25% to 30% more energy from the original uranium in the process and thus contributing to energy security and 2) reduce the volume and radioactivity of the waste by recovering all long-lived actinides and fission products followed by recycling them in fast reactors where they are transmuted to short-lived fission products; this reduces the volume to about 20%, reduces the long term radioactivity level in the high-level waste, and complicates the possibility of the plutonium being diverted from civil use – thereby increasing the proliferation resistance of the fuel cycle.

In a nuclear power plant for energy production, fuel elements are removed from the reactor before the fissile material has been completely consumed, primarily because of fission product buildup. Fission products capture large numbers of neutrons, which are necessary to sustain a chain fission reaction. As a result, only 5 to 10% of the available energy has been expended in the fissile material. Recycling the spent nuclear fuel could produce hundreds of years of energy from the already mined uranium. All commercial reprocessing plants use the well-proven aqueous (hydrometallurgical) PUREX* process. This process involves

* * PUREX is an acronym standing for Plутonium-Uranium Recovery by EXtraction

dissolving the spent nuclear fuel elements in concentrated nitric acid. Solvent extraction steps are then used for the chemical separation of uranium and plutonium from the fission products. Neptunium, which may be used for producing ^{238}Pu for thermo-electric generators for spacecraft, can also be recovered if desired. The plutonium and uranium can then be returned to the input side of the nuclear fuel cycle – the uranium to the conversion plant prior to re-enrichment and the plutonium straight to mixed oxide (MOX) fuel fabrication; typical MOX reactor loading is ~30% MOX fuel elements. [Gray 2012, DOE/EM 1997, Campbell and Burch 1990, Cleveland 1970, Cleveland 1979, Gray 1986, McKibben 1984, Cleveland 1980, Zenter 2005, WNA 2015, Simpson 2010, Gray 1993, Irish 1957, Gerber 1993, Lawroski 1957, Howells 1958, Hinton 1957, Ross 1957, Thompson and Seaborg 1957a, Thompson and Seaborg 1957b, Hamaker 1943, Gofman 1995, Hecker 2006, Wymer and Vondra 1981, Long 1978, Flanary 1956, Cooper 1958, Stoller 1961, Bruce 1956, Bruce 1958, Bruce 1961, Martin 1958, Proceedings Geneva 1956, Proceedings Geneva 1958, Flagg 1961, Brussels Symposium 1963, Starks 1977, Irish 1957a, Irish 1957b, WNA 2015, Schneider and Marignac 2008]

In a plutonium production plant, fuel elements or target are removed when the desired plutonium isotopic concentration is reached.

- To be used in a nuclear weapon[†], plutonium must be separated from the much larger mass of non-fissile material in the irradiated fuel. After being separated chemically and reduced to the metallic state, the plutonium is immediately ready for fabrication into a nuclear explosive device.
- To be used in physics experiments[‡], the plutonium may be converted either to oxide or to metal.

Reprocessing plants in the West and Japan are generally characterized by heavy reinforced concrete construction to provide shielding against the intense gamma radiation produced by the decay of short-lived fission product isotopes.

Plutonium and uranium reprocessing (extraction, separation, purification, isolation, and finishing as oxides) are generally combined in the same facility in the civilian nuclear fuel cycle. This co-location is not necessarily the case in weapons plants.

[†] Weapons grade plutonium is typically defined either as super grade, less than 3% ^{240}Pu , or military grade, less than 7% ^{240}Pu . Various countries define reactor grade plutonium as greater than either 18 or 19% ^{240}Pu .

[‡] Depending on the experiments to be performed, the isotopic may be fuels grade, typically 7 to ~ 18 or 19% ^{240}Pu , or may be much higher than reactor grade.

In general, reprocessing schemes can be divided into two large categories:

- A. Aqueous/hydrometallurgical systems, and
- B. Pyrochemical/pyrometallurgical systems

Worldwide processing schemes are dominated by the aqueous (hydrometallurgical) systems. In general, the aqueous systems can be divided into the following general unit operations:

1. Head end
2. Separations and purifications
3. Concentration
4. Isolation
5. Finishing to desired products

Only a few of the pyrochemical/pyrometallurgical systems have progressed to the pilot plant stage of development. A few of these will be discussed from the standpoint of plutonium recovery.

I.A Review Of Aqueous (Hydrometallurgical) Systems

Of all separation techniques that have been applied to actinide separations from the fission products, solvent extraction offers the greatest number of options and adjustable parameters to fine-tune performance. Further, it is perhaps the separations technique best adapted to the continuous operations, high throughput, and remote handling that are essential to the production-scale processing of spent nuclear fuels. It is possible to vary operating conditions (such as temperature, reduction/oxidation (redox) reagents, solution concentrations, etc.) over rather wide ranges with only minor changes in the final outcome. For this reason, operating practices vary not only among different nations, but also among different plants within a nation. [Gray 2012, McKibben 1984, Simpson 2010] In a few cases, uranium was either not recovered[§] or was recovered and not purified,^{**} but left for subsequent recovery or purification, if desired.

[§] The original processes at the Hanford Works discarded the uranium directly to waste. In later years much of the uranium was recovered from the waste tanks.

^{**} North Korea recovered and separated the uranium from the plutonium, but simply stored the separated uranium solution without purification. [Hecker 2006]

The process variations reported here should be considered to be typical of industrial scale; they are not necessarily optimum flowsheets. Any attempt to cover all the possible process variations would be impossible within space limitations of this chapter. More complete discussions of various flowsheets and processes are presented elsewhere [Stoller 1961, Bruce 1956, Bruce 1958, Bruce 1961, Martin 1958, Proceedings Geneva 1956, Proceedings Geneva 1958, Flagg 1961, Brussels Symposium 1963, Lawroski 1957]

In today's world, the requirements for reprocessing can be stated qualitatively:

- Uranium and plutonium should be as free as possible from attendant chemical impurities and radioactivity-purity is sufficiently high enough that these elements can be used for their intended purposes.
- Losses of uranium and plutonium should be as small as possible-typically a few tenths of 1% to 1% (for example France and Russia strive to maintain their losses to the waste streams to less than 0.1 %).
- Impact on the environment from the entire operation, now and for all time to come, should be minimized.
- Laws of economics are applicable in the final decisions as to exactly which flowsheet and process chemicals are to be used.

Clearly, as with any industrial operation, trade-offs must be made. [Wymer and Vondra 1981]

Plutonium separations and purification are effected by chemical means, which are possible because plutonium displays different chemical behavior than the other approximately 35 elements (about 30 fission products [Hammer 1943, Gofman 1995] and other actinides in the spent nuclear fuel as well as chemical reagents used in processing) with which it is mixed in a spent fuel tube or plutonium production target. Because the process involves separating different elements rather than separating isotopes of a specific element, it is technically easier, in principle, to separate uranium from plutonium than to enrich uranium with respect to a given isotope. But the processing of freshly irradiated spent nuclear fuels or targets is made more difficult by the intense radiation emanating from the commingled fission products. [Bunn and Weir 2006]

Currently, all of the major processing plants use solvent extraction to separate plutonium from uranium and from fission products. [Cleveland 1980, McKibben 1983, Gray 2012, WNA 2015] These solvent extraction processes yield

plutonium and uranium separated from each other and from approximately 30 fission products present in the spent nuclear fuel. The overall process can generally be divided into five segments:

- 1) Head-end operations: Preparation of the spent nuclear fuel for dissolution and its subsequent dissolution vary widely depending on chemical composition of the fuel meat and cladding. Typically the preparation involves some degree of disassembly followed by fuel meat exposure: This disassembly may involve shearing or chopping or it may involve mechanical or chemical decladding. Once exposed, the fuel meat is typically dissolved in concentrated nitric acid.
- 2) Separations and decontamination or purification: In the separation of uranium and plutonium from each other and from fission products^{††}, all commercial reprocessing plants have used solvent extraction; early reprocessing plants for weapons materials had used precipitation but all of them were converted to solvent extraction.
- 3) Concentration: Volume reduction by ion exchange or evaporation.
- 4) Isolation: Separation of the plutonium from solution via precipitation.
- 5) Conversion to final product: The recovered and purified uranium and plutonium may be finished either as oxides (for use in MOX fuel or physics experiments) or as a metal (for use in nuclear weapons or physics experiments).

A wide variety of chemistries can be used for these operations depending upon the scale of operations. A particular operation that is useful for the gram or sub-gram level may or may not be appropriate for the kilogram level. As this chapter deals with recovery of plutonium from spent fuels and targets, this chapter details only with those chemistries used for industrial scale operations. Other chapters should be consulted for the detailed chemistries that may be used for smaller scale of operations and for the detailed chemistries upon which these production-scale separations processes are based.

All of the production scale solvent extraction plutonium separations processes have been based on three factors:

1. The ease of adjusting the oxidation state of plutonium between Pu(III), Pu(IV) and Pu(VI) [PuO_2^{2+}] in the presence of hexavalent uranium, UO_2^{2+} ,

^{††} Fission products are discarded as waste. If other actinides are present, e.g. neptunium, americium, or curium, they may be recovered either as their respective oxides or rejected to the waste stream.

- especially the ease of reducing plutonium selectively to the trivalent state or stabilized in the tetravalent state.
2. The ability of Pu(IV) to form cationic, neutral, and anionic complex ions with the nitrate ion; Pu(III) does not form these complexes.
 3. The high extractability of the higher valencies of plutonium and uranium into an organic phase but the inextractability of the trivalent ions of plutonium into that organic phase.

Whereas the PUREX^{‡‡} Process has been the dominant separation process to separate plutonium from commercial spent fuel, [McKibben 1983] seven processes have been used in weapons programs to separate weapon plutonium from irradiated fuels and targets. Two of these processes were precipitation processes; four processes were solvent extraction processes; and one was a mixture of solvent extraction and precipitation. [Gray 2012] The original processes in the United States, the Soviet Union and China were carrier co-precipitation processes: the United States used the Bismuth Phosphate Precipitation Process; [DOE/EM 1997, Thompson and Seaborg 1957a, Thompson and Seaborg 1957b] the Soviet Union scaled up an old quantitative analytical precipitation procedure based upon sodium uranyl acetate precipitation. [Gray 1993, Gray 1999] (This procedure was originally used at the University of California Berkeley to isolate the first milligram amount of ²³⁹Pu. [Hamaker 1943, Gofman 1995]) With help from the Russians, the Chinese also initially used the sodium uranyl acetate co-precipitation process. Since the Bismuth Phosphate Process was a batch process, generating tremendous volumes of waste^{§§} and the uranium was not recovered, the United States moved to a continuous solvent extraction process – the REDOX^{***} Process with methyl isobutyl ketone (hexone) as the solvent and aluminum nitrate as the salting agent. [Irish 1957, Gerber 1993, Lawroski 1957] The REDOX Process also generated large amounts of waste due to the aluminum nitrate salting agent^{†††} so it was replaced with the PUREX Process, which used nitric acid as the salting agent (which could be distilled and recycled) and 30% tri-n-butyl phosphate

^{‡‡} PUREX is an acronym standing for **P**lутonium-**U**ranium **R**ecovery by **E**Xtraction

^{§§} During the 1940s and 1950s, the bismuth phosphate process used in T and B Plants at Hanford generated an average of 30 cubic meters of waste per metric ton of spent fuel processed. [Gephart 2003]

^{***} REDOX is an acronym that stands for **RED**uction **OX**idation

^{†††} Initially, the hexone solvent extraction process used in the REDOX Plant at Hanford generated 15 cubic meters of waste per ton of spent fuel processed. Process improvements reduced this to 2 cubic meter of waste per metric ton of fuel processed. [Gephart 2003]

(TBP) diluted in a normal paraffin hydrocarbon (originally kerosene-type diluents) as the solvent.^{†††}

The Canadians and the British developed two solvent extraction processes: the BUTEX Process and the TRIGLY Process. [Hinton 1957, Ross 1957, Cleveland 1980, Cleveland 1979] The BUTEX Process utilizes two solvents: undiluted dibutyl carbitol (butex) for separations of the fission products and plutonium from uranium, and then 20% TBP in kerosene for plutonium purification. The TRIGLY Process (used for only a very short time; the extractant did not recover uranium, and plutonium recovery was poor) used triglycol dichloride for the first extraction cycle followed by a cycle using methyl isobutyl ketone (hexone) and thenoyl trifluoroacetone (TTA). Additionally, the TRIGLY Process alternated between solvent extraction and precipitation creating a very complex process.

France originally developed a different version of PUREX Process, which utilized TBP for the primary separation followed by a plutonium concentration stage utilizing co-precipitation of plutonium and uranium using sodium carbonate. France and the Democratic People's Republic of Korea (North Korea) have used an intermediate step of anion exchange to both concentrate and further purify the plutonium stream. The United States, at the Savannah River Site, used cation exchange to concentrate the plutonium product. Most other plants have used evaporation to concentrate the plutonium. All plants have used evaporation to concentrate the uranium stream. Virtually all of the different processing plants now use the PUREX Process to recover and purify their actinide products. The equipment used for separation and purification process and operations have been vastly different from nation-to-nation as well as from plant-to-plant within the same country.

As the PUREX Process is the most important process, it is covered in much greater detail than the earlier processes; the earlier processes are covered primarily because of their historical interest.

All seven of these separation processes are based on the ease of adjusting the valence of plutonium between the Pu(III), Pu(IV) and Pu(VI) oxidation states in the presence of U(VI). Each of these processes differs in many respects. The

^{†††} Depending upon the fuel reprocessing campaign, the PUREX Process generate 5 cubic meters to less than 1 cubic meter of waste per metric ton of fuel processed. [Gephart 2003]

precipitation processes were based on the carrying of Pu(IV) or Pu(VI) but not Pu(III). The solvent extraction processes were based on the selective extraction of Pu(IV) and the inextractability of Pu(III).

In general, all commercial reprocessing plants concentrate their plutonium via evaporation and finish their plutonium either as PuO₂ or as a mixture of UO₂-PuO₂. [Gray 2012, Long 1978, WNA 2014] In the United States, the first commercial reprocessing plant was at West Valley, New York. It had a capacity of 300 tonne/year and was operated successfully from 1966-72. However, escalating regulation required plant modifications, which were deemed uneconomic, and the plant was shut down. The second commercial reprocessing plant also had a 300 tonne/year capacity and was built at Morris, Illinois, incorporating new technology which, although proven on a pilot-scale, failed to work successfully in the production plant. It was declared inoperable in 1974. The third commercial reprocessing plant had a capacity of 1500 tonne/year and was built in Barnwell, South Carolina. It was never completed due to a 1977 change in government policy, which ruled out all U.S. civilians reprocessing as one facet of U.S. non-proliferation policy. In all, the United States has over ~250 plant-years of reprocessing operational experience, the vast majority being at government-operated plants since the 1940s for weapons programs. The weapons plants have used a variety of chemical processes to concentrate (e.g., evaporation, cation exchange, or anion exchange) their plutonium streams and to convert the plutonium to metal.

Sidebar

Objectives of the Separations Processes

The original object of the US chemical processes was to separate and recover the plutonium. The plutonium existed in the irradiated rods only to the extent of about 300 parts per million, a concentration which would be considered to be no higher than impurity level in normal extraction chemistry. The secondary, but not original, object was to extract uranium so that it can be purified, re-enriched, and used once more in fuel elements. The fission products, which comprise some 30 elements in the middle of the periodic table, are generally beta and gamma emitters and vary widely in chemical character. They include the rare gases krypton and xenon, the rare earths and (an important factor) radioactive iodine. The half-lives vary from seconds to years and daughter products are formed by decay, thereby increasing the complexity of the chemistry. In general the flowsheet targets had a recovery efficiency of 99.9% and a decontamination factor from other radioactive isotopes of 10^8 .

[Hamaker 1943, Gofman 1995]

The PUREX process has also been modified to recover other products. These modified processes include the HM Process (H-Area modification) to recover enriched uranium and neptunium, J-Cell at the Hanford PUREX to recover neptunium, the THOREX^{§§§} and Acid THOREX processes to recover ^{233}U from thorium fuels and the TRAMEX^{****} or TRUEX^{††††} Processes to recover ^{252}Cf , ^{244}Cm , ^{243}Am and high plutonium isotopic (HPI) material from plutonium targets. These processes will also be covered briefly.

I.B Review of Pyrochemical/Pyrometallurgical Systems

§§§ THOREX is an acronym that stands for **THO**rium **R**ecovery by **EX**traction

**** TRAMEX is an acronym standing for **TR**ans**A**mericium **EX**traction

†††† TRUEX is an acronym standing for **TR**ans**U**ranic **EX**traction

The economic incentive of avoiding the waste generated by aqueous processing has led to the proposal of a number of pyrochemical and pyrometallurgical flowsheets, only a few of which have progressed to the pilot plant stage of development. [Cleveland 1980, Madic 2000, Nash 2006, IAEA 2010] All the pyrochemical processes use halide salts as electrolytes for partitioning the useful elements such as uranium and plutonium from spent nuclear fuels. Alkali, alkaline earth, and some of the rare-earth fission products accumulate in the molten salts. Replacement with a clean electrolyte instead of reuse of electrolyte from pyrochemical process is widely adapted. The chemical/physical form of waste from pyrochemical process depends on the original electrolyte used in the process. [IAEA 2010, Madic 2000, Nash 2006] Some of these processes will be discussed from the standpoint of plutonium recovery.

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II. AQUEOUS (HYDROMETALLURGICAL) SEPARATIONS PROCESSES

In general aqueous (hydrometallurgical) separations processes can be divided into two broad categories:

1. Solvent Extraction Processes
2. Precipitation Processes

II.A PUREX and Modified PUREX Processes

Successful solvent extraction processes depend on the selective transport of the target metal ion (or group of metal ions) from an aqueous solution containing

contaminants into an immiscible organic solution. When the target metal ion is removed from that organic phase, it will have undergone some degree of purification, often characterized in terms of a ‘decontamination factor’ (DF). Of all separation techniques that have been applied for actinide separations, solvent extraction offers the greatest number of options and adjustable parameters to fine-tune performance. Further, it is perhaps the separations technique best adapted to the continuous operations, high throughput, and remote handling that are essential to the production-scale processing of spent nuclear fuels. A variety of solvent extraction processes have been used to separate and purify plutonium and uranium. [Nash 2006] The major processes are covered below.

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II.A. 1 Overview of The PUREX Process

The most used target/spent fuel reprocessing technology in the world today is the PUREX Process and is the standard method of plutonium/uranium separations worldwide. [McKibben 1984, Gray 2012] A generic flowsheet of this liquid-liquid extraction process is given in Figure XXX. The concept and early development of the process occurred at the Knolls Atomic Power Laboratory (KAPL) in 1950, demonstrated in a pilot plant at the Oak Ridge National Laboratory in 1952, and put into initial production in the F-Area Canyon (Processing Building 221-F) at the Savannah River Site in 1954. [McKibben 1984] The PUREX Process replaced the REDOX process at Hanford in January 1956^{***}. [Gray 2012, DOE/EM 1997] The Soviet Union had converted all three of its co-precipitation processes to the PUREX Process by 1972. [Gray 1993]

^{***} Hanford operated both the PUREX process and the REDOX Process for a number of years. The REDOX Plant was actually shut down in December 1967. [DOE/EM 1997]

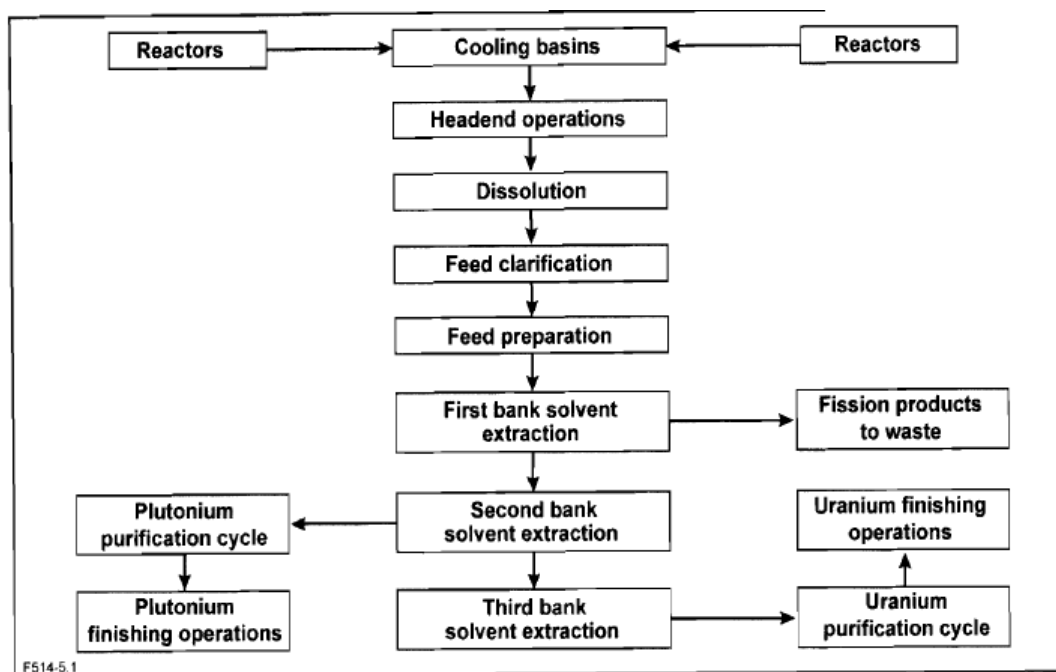


Figure XXX. Generic PUREX Process Flowsheet

The extractant selected was tri-n-butyl phosphate (TBP), which has proven to be an excellent choice. [Gray 2012, DOE/EM 1997, Campbell and Burch 1990, Cleveland 1970, Cleveland 1979, Gray 1986, McKibben 1984, Cleveland 1980, Gray 1998, Gray 1993, Zenter 2005, Simpson 2010, Long 1978, Logsdaile 1985] TBP has good radiolytic and chemical stability, low aqueous solubility, and its chelating properties make it possible not only to efficiently eliminate undesirable fission products and other actinides activation-products (e.g., neptunium, americium, curium), but also cleanly separate the two desired products – uranium and plutonium – from each other. This separation is accomplished by the selective removal of both plutonium [as Pu(IV)] and uranium [as U(VI)] from dissolved spent fuel solutions (3–6 M HNO_3) as their electroneutral nitrate salts with minimal complication into the TBP. (See Figure XXXX) However, the density of TBP (0.98) is so close to water that a dilution in a non-polar, low-density organic liquid is necessary to achieve adequate phase separation. Due to the chemical and radiolytic degradation of branched chain hydrocarbon, straight-chained hydrocarbon solvents are the best diluents for TBP: n-dodecane is the best solvent but ultrasene, kerosene, odorless kerosene (or OK, which is oleum-washed kerosene), distilled coconut oil, mixtures of straight chain alkanes from 12 to 16 carbons and shellac-thinner have been used. [McKibben 1983, Gray 2012]

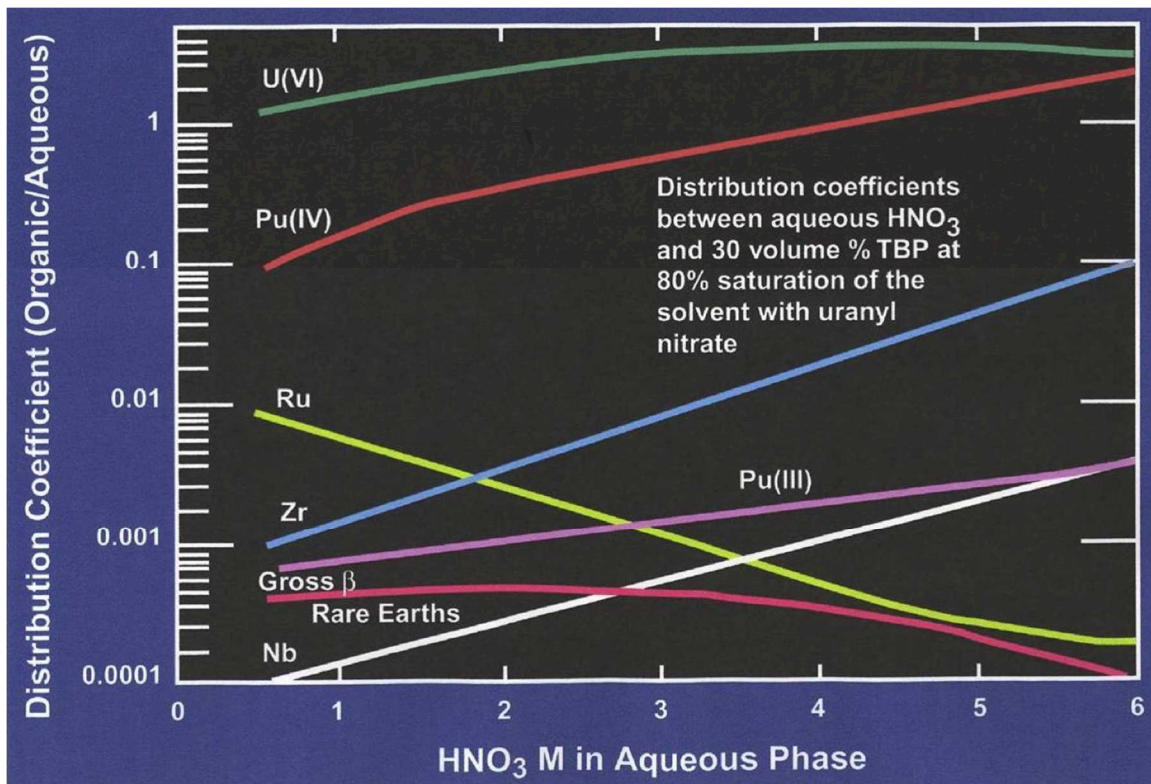


Figure XXXXXX Extraction of actinides into tri(n-butyl)phosphate in dodecane as a function of nitric acid concentration

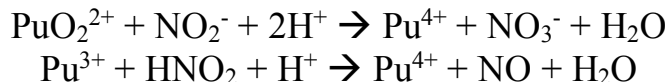
II.A.2 Generic PUREX Process Flowsheet

The typical Purex aqueous feed contains uranyl nitrate, nitric acid, plutonium nitrate, fission product nitrates, and small concentrations of actinide activation-products (primarily $\text{Np}^{\text{§§§§}}$, Am, and Cm, amounts depending upon the fuel burnup). [Gray 2012, DOE/EM 1997, Campbell and Burch 1990, Cleveland 1970, Cleveland 1979, Gray 1986, McKibben 1983, Cleveland 1980, Zenter 2005, Simpson 2010, Irish 1957] The organic feed is typically 30% TBP in one of the above diluent, although 3%, 7.5%, 10%, 20%, and even 50% TBP have been used for certain applications.

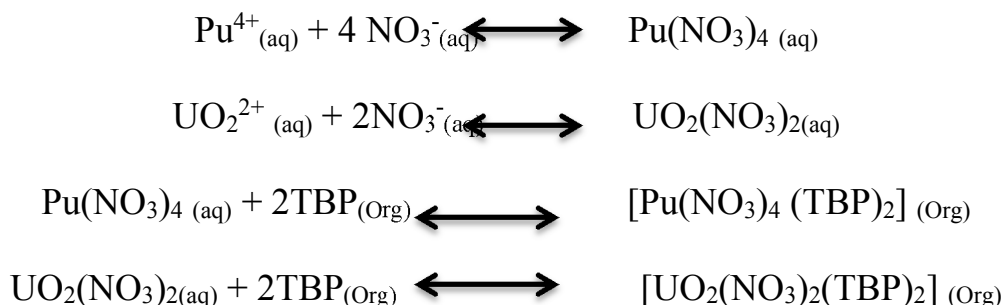
The most efficiently extracted plutonium species is the tetravalent state (see Figure 28. XXX above). When necessary, the feed solution, containing plutonium, uranium, minor actinides, and fission products, is treated with nitrite

§§§§ Neptunium, which can be used to produce ^{238}Pu for use in thermo-electric generators, can be recovered if so desired.

ion (either as a salt, NaNO_2 , or as a gas, NO_2) to convert all plutonium to the tetravalent state by the following equations: [Cleveland 1980, Irish 1957, Cleveland 1979]



The reaction is rapid, being complete in a few minutes. Plutonium and uranium are then extracted into the organic phase, leaving the bulk of the fission products and minor actinides in the aqueous phase. [Cleveland 1980]



Plutonium can then be back-extracted or stripped from the TBP phase by reduction of the Pu(IV) to Pu(III) with an aqueous solution of dilute nitric acid and ferrous sulfamate:



Ferrous ion serves as the reductant, with sulfamate, acting as a holding reductant, reacts with nitrite, which extracts along with the plutonium:



If a holding reductant were not present the nitrite would autocatalytically oxidize the ferrous ion and prevent the reduction of plutonium. A several-fold excess of ferrous sulfamate is used to ensure complete reduction. Because uranium is not reduced by the ferrous sulfamate, it remains in the organic phase. [Wick 1970, Wick 1979]

The overall PUREX process typically includes a head-end and three separate solvent-extraction cycles(See figure XXXX): [McKibben 1983, Gray 1986, Gray 2012, DOE/EM 1997]

A. The head-end operation exposes the fuel meat, which is dissolved or

leached from the cladding.

- a. The fuel cladding may be dissolved^{*****}, mechanically removed^{†††††}, or the fuel pins may be chopped or sheared into pieces.^{‡‡‡‡‡}
 - b. The fuel meat is dissolved, or leached from the hulls, typically using concentrated using nitric acid.
- B. There are three cycles of solvent extraction which perform the following:
- a. In the first cycle, uranium and plutonium are co-extracted into an organic phase, leaving the fission products and other actinide activation products in the aqueous phase^{§§§§§}. Neptunium, a by-product of the irradiation of ^{238}U , can be rejected to the aqueous waste stream, if desired, by feeding a small stream of nitrous acid or nitrite salt into the bank to keep the neptunium in the inextractable Np(V) valence.^{*****}
 - i. Pu(IV) and U(VI) cations form stable, neutral nitrate complexes that are selectively extracted into the organic phase whereas fission products cations generally do not form neutral nitrate complexes and therefore are not extracted into the organic phase.
 - b. In the second cycle, plutonium is stripped away from the uranium and returned to an aqueous phase.
 - i. This separation is based on the selective reduction of the Pu(IV) to the inextractable Pu(III) state; the nitrate concentration is kept high enough so that the neutral uranyl nitrate complex does not decompose. Therefore, the uranium remains in the organic stream.
 - c. In the third cycle, uranium is stripped away from the organic phase into dilute nitric acid.
 - i. The nitrate concentration is lowered sufficiently that the neutral uranyl nitrate complex decomposes and the uranium

^{*****} Aluminum cladding is typically dissolved using NaOH- NaNO_2

^{†††††} The British and the French typically mechanically removed the Magnox fuel cladding.

^{‡‡‡‡‡} Commercial spent fuels are typically sheared into short pieces prior to leaching with concentrated nitric acid.

^{§§§§§} Typically about 3% of the fuel has been converted to fission products and the minor actinides Np, Am, and Cm.

^{*****} The RT-1 facilities at Krasnoyarsk-26 and the HM process in H-Area at Savannah River recover the Np.

thus strips into the aqueous phase.

- C. An additional solvent-extraction cycle further purifies the plutonium from additional fission products.
 - a) The plutonium valence must be adjusted from Pu(III) to Pu(IV) prior to feeding to the first bank.
 - b) In the first bank, the plutonium is extracted away from
 - i. Additional fission products,
 - ii. Chemicals used to strip the plutonium from the first cycle organic phase and
 - iii. Chemicals used to prepare the feed for the second cycle.
 - c) In the second bank, the plutonium is reduced to the Pu(III) state and stripped from the organic phase back into an aqueous phase by reduction with hydroxylamine nitrate or hydrazine to avoid undesired impurities; the plutonium is now ready for the finishing operations.
- D. A second two-bank solvent-extraction cycle further purifies the uranium from additional fission products.
 - a. The uranium is first concentrated via evaporation to prepare it as feed for the second purification cycle.
 - b. In the first bank, the uranium is extracted away from residual fission products.
 - c. In the second bank, the uranium is stripped from the organic phase back into an aqueous phase; the uranium is now ready for the finishing operations

The only fission products that are sufficiently extractable to become significant contaminants in the product streams are ^{95}Zr , ^{103}Ru , and ^{106}Ru . These fission products have short enough half-lives (^{95}Zr $t_{1/2}= 65.5$ d; ^{103}Ru $t_{1/2}= 39.5$ d; ^{106}Ru $t_{1/2}= 368$ d) that they typically are not a problem in commercial fuels cooled for four years or more. [McKibben 1983] However, ^{93}Zr ($t_{1/2}=1.5 \times 10^6\text{y}$), ^{99}Tc ($t_{1/2}= 2.12 \times 10^5$ y), thorium, neptunium, and the trivalent actinides are detectable by radiochemistry means in gram-sized samples. [Moody 2005]

A typical plant-scale performance of a two-cycle PUREX process is given in Table XXX. [Cleveland 1979, Irish 1959]

Table XXX. Typical plant-scale performance of two-cycle PUREX process

Process	Decontamination Factor
Separation of uranium from plutonium	$>10^7$
Separation of plutonium from uranium	10^6

Decontamination of fission products from plutonium	$> 10^8$
- First cycle decontamination factor	2×10^4
- Second cycle decontamination factor	2×10^3
Decontamination of fission products from uranium	10^7
- First cycle decontamination factor	2×10^4
- Second cycle decontamination factor	5×10^2
Plutonium and uranium recovery, %	99.9
Acid recovery – solvent extraction, %	95
Solvent recovery, %	99.7

II.A.3 Other Reductants Used for PUREX Processing

Ferrous sulfamate is perhaps the most commonly used reductant for stripping plutonium from uranium and fission products in the organic phase. [Gray 2012, DOE/EM 1997, Campbell and Burch 1990, Cleveland 1970, Cleveland 1979, Gray 1986, McKibben 1984, Cleveland 1980, Zenter 2005, Simpson 2010, Irish 1957, Gerber 1993, Long 1978, Logsdaile 1985] However, ferrous sulfamate has the disadvantage that it introduces iron and sulfate into the system, which increases the waste volume that must be stored.

Therefore other flowsheets have been developed to reduce plutonium (IV) to plutonium (III). For example, U(IV)-hydrazine can be added as a solution of 1.5 to 2.0M HNO_3 or produced electrochemically in the equipment.



Hydrazine plays the same role as sulfamate ion in destroying the HNO_2 in accordance with the equation



Followed by



Unreacted U(IV) and the reaction product UO_2^{2+} are extracted into the organic phase, leaving behind Pu(III) of sufficient purity in the aqueous phase. However,

U(IV) has the potential disadvantage of requiring the reductant uranium to have the same isotopic composition as the uranium being processed.

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II.A.4 Modifications of PUREX Used at Plant Scale

II.A.4.1 The French Version of PUREX

The main French facility for the production of plutonium for military purposes is the complex located at Marcoule. [NWA 2001b, NWA 2001a, F. G. 1960, 1984, WMD-Marcoule] The facility was conceived in 1952. Plans were begun in June 1954; work on the plant began a year later. Dry runs began by the end of 1957 and processing of the first load of irradiated uranium began on 6 July 1958. The facility had France’s first plutonium production reactor, a natural uranium fueled, graphite moderated, gas-cooled G1 reactor (a MAGNOX reactor) and its first plutonium separation plant, known as Usine de Plutonium, or Plutonium Factory (UP1). In February 1996, the French President announced that France had sufficient fissile materials and that processing of plutonium would cease when processing of spent fuel from gas-cooled reactors was completed near the end of 1997. [WMD-Marcoule]

After mechanical decladding, the fuel meat was dissolved in 11N HNO₃ at the boiling point. Extraction was done in three stages. The first stage (see figure XXX) was typical TBP (20% TBP by volume) extraction of the uranium and plutonium followed by a second stage in which plutonium was stripped using uranium(IV) sulfate. The plutonium was then concentrated using sodium carbonate precipitation. First sodium carbonate was added to the decanter, followed by the dilute plutonium solution. A predetermined quantity of uranium was added as uranyl nitrate; next by adding nitric acid the pH was adjusted from about 12 to 10.8. After decanting, the precipitation operation was repeated six times before the whole precipitate was dissolved in nitric acid. This processing yielded a solution containing 5 to 10 grams of plutonium per liter and 70 to 80 grams of uranium per liter.

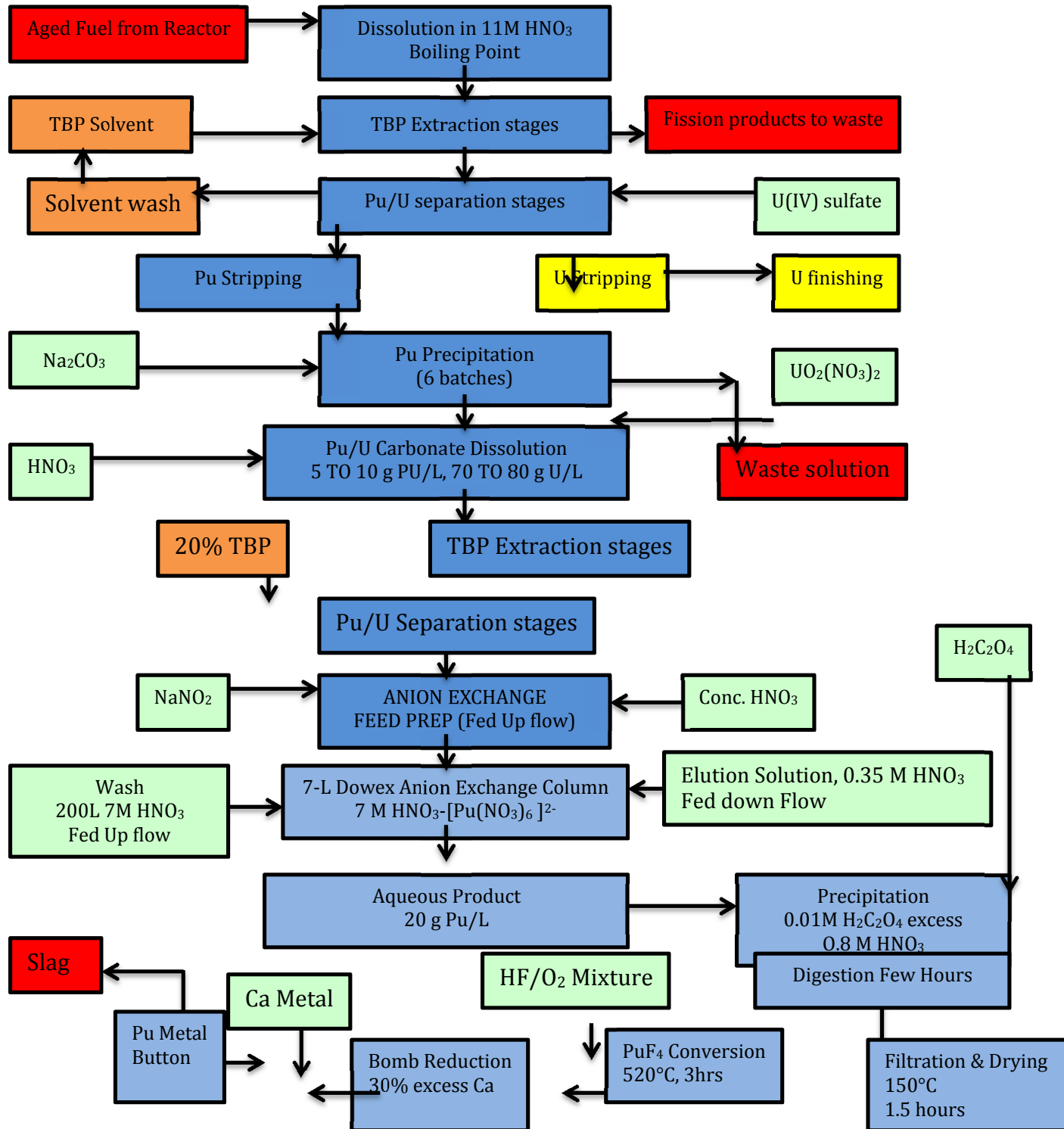
This solution was then extracted with 20% TBP and the plutonium stripped using ferrous sulfamate. The plutonium valence was adjusted using sodium nitrite; the nitric acid adjusted to 7N with concentrated nitric acid and then fed up-flow to Dowex anion exchange resin. The column was washed up-flow with 7N nitric acid (about 30 column volumes) and eluted down-flow with 0.35N nitric acid, yielding a solution of about 20 g Pu/L. Plutonium was then converted

to Pu(IV) oxalate by adding oxalic acid to the plutonium solution to yield a 0.01 N excess; the final nitric acid concentration at the end was about 0.8 N.

Conversion to metal was in approximately 100-gram plutonium oxalate batches. The plutonium oxalate was first dried in air at 150°C for 1.5 hours followed by fluorination at 520°C in a stream of mixed HF and O₂ gas. The resulting PuF₄ was then mixed with 30% excess Ca and reduced to plutonium metal in a sealed pressure vessel.

France later converted to the more-or-less standard PUREX flowsheet.

FIGURE 28.XXXX. ORIGINAL FRENCH VERSION OF PUREX



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II.A.4.2 Modification to Recover $^{233}\text{U}/\text{Th}$

II.A.4 .2.1 THOREX Process

In the 1960s and 1970s, there was great interest in development of the thorium fuel cycle to supplement the uranium reserves. The recovery of ^{233}U from thorium-based fuel is accomplished using a process similar to PUREX, called THOREX (**THOR**ium **EX**traction). [Orth 1979, Moody 2005, Long 1978, Palamalai 1994, Prout 1967, Gresky, 1956, Haas 1956, Morgan 1958, Rainey 1958, Nash 2006] Even though the THOREX process can claim a more or less similar history of as the PUREX Process, it cannot claim the same robustness as that of the latter process . Most of the experience in THOREX Process domain has come from the recovery of low amounts of ^{233}U bred in irradiated ThO_2 .

The (n, 2n) reactions encountered during the irradiation of thorium lead to the formation of long-lived ^{231}Pa and relatively short lived ^{232}U (68.9 yrs.), and its hard beta, gamma emitting daughter products. Thus the ^{233}U produced in the reactor is contaminated with ^{232}U and the level of contamination depends on the

isotopic composition of initial thorium fuel, the burn-up, and the neutron spectrum encountered in the reactor. The radioactive contamination from ^{232}U in the separated ^{233}U product and from ^{229}Th and ^{228}Th in the separated THOREX products will have to be taken into consideration when handling these products. In general, reactor fuel elements containing ^{233}U may be fabricated semi-remotely provided that complete fabrication can be accomplished in two weeks or less. If ^{233}U contains more than 200 ppm ^{232}U , or if re-fabrication of fuel elements requires longer than two weeks, a shielded re-fabrication facility is necessary. Thorium fuels must be allowed to decay for 12 years if unshielded re-fabrication procedures are to be used.

A typical flow sheet for the processing of thorium (as thoria, ThO_2) irradiated in power reactors for ^{233}U separation used TBP. The ^{233}U was preferentially extracted leaving the bulk of thorium in the raffinate. The extraction was carried out in the presence of fluoride and aluminum ions. Five thorium-processing campaigns were conducted at the Savannah River Plant. Two different flow sheets were used and a total of about 240 metric tons of thorium and 580 kg of uranium were processed. In the first two campaigns on thorium oxide, uranium was recovered with a dilute 3.5% TBP flow sheet and the thorium was sent to waste. The ^{232}U concentrations in these two campaigns were 40–50 ppm and 200 ppm. In the third campaign, THOREX was used to process thorium metal and thorium oxide. ThO_2 was processed in the final two THOREX campaigns. The three THOREX campaigns used 30% TBP to recover both uranium and thorium. Irradiation conditions were set to produce a concentration of 4–7 ppm ^{232}U . [Rainey and Moore 1962, Orth, 1978, Watson and Rainey 1979a,b]

Different flow sheets have been used to meet the specific requirements of fuel from different reactor systems based on the type of ThO_2 target/fuel and the cladding under treatment, its irradiation, and cooling history and the end objectives of the processing and the final product decontamination factor desired. As with PUREX, processing must allow a decay time interval to allow the long-lived ^{233}Pa , $t_{1/2} = 27\text{d}$, to decay to desirable product ^{233}U . [Moody 2005]

The separation of thorium from uranium is most typically accomplished using the same basic chemistry that drives the PUREX process, i.e. extraction of Th(IV) and U(VI) from nitric acid solutions into TBP solutions with aliphatic hydrocarbon diluents. The use of an acid deficient feed (0.15 M) induces high decontamination while injection of HNO_3 at the fourth extraction stage provides high salting strength and ensures quantitative uranium and thorium extraction.

Because thorium is extracted by TBP less effectively than Pu(IV) or U(VI), the introduction of $\text{Al}(\text{NO}_3)_3$ [Oliver, 1958] or $\text{Be}(\text{NO}_3)_2$ [Farrell et al., 1962] as salting out reagent has been demonstrated.

A typical flowsheet is given in Figure 28.XXXXXX

Figure 28.XXXXXX

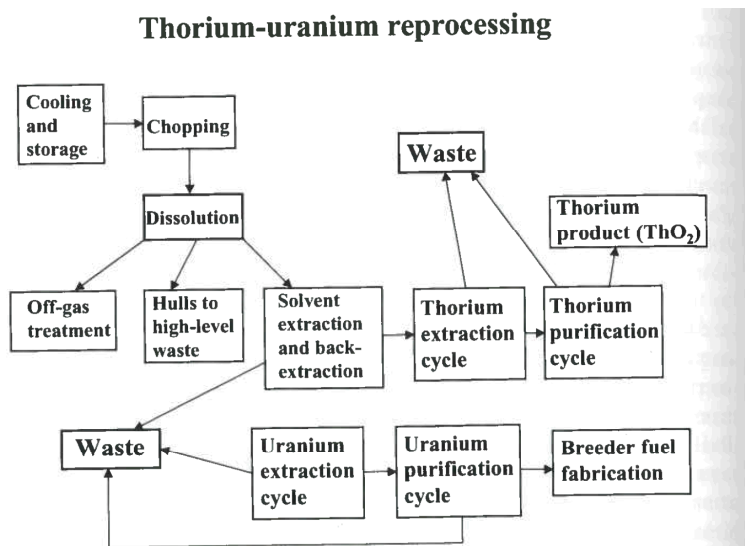


Figure 3.23 Flow diagram for a Th-U reprocessing facility. The basic operations are similar to those outlined in Figure 3.22 for the U-Pu process. The main difference is that U is the fissile component rather than the fertile component, so more care must be taken for more efficient recovery. The usual process is THOREX.

A large potential also exists for resources conservation through introduction of thorium fuel cycles in CANDU (CANada Deuterium Uranium) reactors. The THOREX Process uses n-tributyl-phosphate (TBP) in normal paraffin hydrocarbon (NPH) as the extractant. The main difference compared to PUREX is that the valuable fissile material is ^{233}U , which is the main product stream, as opposed to that of an ancillary side stream. An additional difference is that the complementary actinide thorium can be neither oxidized nor reduced from the Th(IV) oxidation state. In this process, uranium is separated from thorium through exploitation of the difference in equilibrium distributions since no usable valence change is available to aid in this separation.

II.A.4.2.2 Acid THOREX Process

The Acid THOREX Process [Rainey 1962] was developed at the Oak Ridge

National Laboratory on a laboratory scale for recovery of uranium and thorium from spent fuel solutions. The dissolver solution was steam stripped to produce an acid deficient feed that was then treated with bisulfite to decrease the extractability of fission products. The thorium and uranium are extracted by 30% tributyl phosphate (TBP) with only the thorium nitrate and nitric acid as “salting agents.” The resulting organic phased was scrubbed with dilute HNO_3 to improve decontamination. As compared to the present THOREX Process in which aluminum nitrate is employed as a salting agent, a considerably greater reduction in aqueous waste volumes is possible with the Acid THOREX Process. With a synthetic solution of Consolidated Edison Thorium Reactor fuel as feed, uranium and thorium were decontaminated from ruthenium, zirconium-niobium, protactinium, and rare earth elements by factors of 2,000, 30,000, 1,000, and 10^5 , respectively. The concentrated aqueous waste volume was 0.2 liter per kilogram of thorium processed. These values compare favorably with corresponding decontamination factor values for the aluminum-salted THOREX system of 600, 3,000, 3,000, and 2×10^5 and volume of 2 liters of concentrated waste per kilogram of thorium processed.

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II.A.4.3 Modification to Recover HEU/Np: HM Process (H-Area Modification of PUREX)

Construction of the H-Canyon separations facility at Savannah River was completed in 1954. Processing of irradiated depleted uranium fuel using the PUREX flowsheet began in July 1955. The introduction of high enriched uranium (HEU) fuels into Savannah River operations to produce a greater

variety of products required the development of a modified flowsheet to ensure criticality safety during recovery of unburned uranium from spent enriched uranium fuels.

This H-Modified (HM) process was introduced into H-Canyon in May 1959 using a 1.5 % TBP flowsheet, which was later changed to 2.5 %. This process was further modified to use 3.5 % TBP in 1963 to permit recovery of neptunium, as well as HEU. The process was changed to 7.5 % TBP in the 1970's to allow both high and low enriched uranium to be processed by the same flowsheet. This change was necessary for the production of special isotopes, such as ^{238}Pu .

The production of ^{238}Pu required the irradiation of ^{237}Np . The ^{237}Np was produced as a byproduct of the neutron irradiation of either natural or enriched uranium. Irradiated HEU was the feed to the HM Process. The aluminum-clad spent nuclear fuel tubes were dissolved in boiling nitric acid catalyzed with mercuric nitrate. The resulting solution contained a mixture of uranium, plutonium (10-30% ^{238}Pu , isotopes vary with ^{236}U content of the fuel), neptunium, aluminum, and fission products. Typically, the solution was evaporated and clarified by precipitation of MnO_2 , forming a silica-gelatin polymer to remove fission products and silicon, and then centrifuged.

A 7.5% TBP-n-paraffin solvent phase extracted uranium and neptunium. The plutonium, aluminum, and greater than 99% of the fission products were not extracted; they were carried out in the waste stream. Stripping out the neptunium, using a 1.5M nitric acid solution partitioned the neptunium and uranium; about 95% of the neptunium was removed. The uranium was then stripped from the solvent into dilute nitric acid.

After adjustment with nitric acid and ferrous sulfamate, the neptunium was extracted into 30% TBP-n-paraffin and then stripped into diluted nitric acid. Fission products and any residual plutonium were rejected to the waste stream.

The aqueous uranium stream was concentrated, adjusted with nitric acid, and extracted into 7.5% TBP-n-paraffin, while about 3% of the neptunium originally present in the original uranium feed was rejected to the waste stream. This neptunium solution was concentrated and blended with the solution from the initially stripped uranium-neptunium feed solution above. This enriched-uranium pregnant-organic stream was stripped with dilute nitric acid. This uranium product stream was recycled into new fuel tubes after conversion to a uranium-aluminum alloy. The neptunium stream was further purified, converted

to oxide, and fabricated into target tubes for return to the reactor to be transmuted into ^{238}Pu .

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II.A.4.4 Other Modifications of PUREX

II.A.4.4.1 J-Cell Modification at Hanford PUREX

As mentioned previously, irradiating ^{237}Np targets produces ^{238}Pu . The J-Cell modification of the Hanford PUREX plant [Duckworth 1964] added an anion exchange column for neptunium recovery and purification. This application of anion exchange to neptunium purification was novel, as anion exchange was typically used for plutonium purification. The flowsheet was adapted to adsorb neptunium on the column (typically 100 mesh Dowex 21-K) and pass plutonium through as Pu(III). Therefore, the feed was adjusted to 6 M HNO_3 with ferrous sulfamate and hydrazine added to reduce the plutonium to Pu(III) and hold neptunium in the Np(IV) state to absorb onto the resin. Even though the plutonium was in the Pu(III) valence state, enough plutonium would absorb to contaminate the neptunium product. A wash of concentrated nitric acid with additional ferrous sulfamate and hydrazine was used to remove the absorbed plutonium. The wash solution were cooled to 20⁰ C. Further decontamination was done by washing with 8 M HNO_3 at 70⁰ C and sodium fluoride to remove traces of plutonium and remaining fission products. The column would then be eluted with 0.3 M HNO_3 to remove neptunium and the waste streams would be treated with sodium nitrite to destroy the hydrazine and aluminum nitrate to

complex the fluoride prior to returning them to the PUREX back-cycle waste stream.

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II.A.4.4.2 Primary Recovery Column at Savannah River F-Canyon

To allow recover of plutonium losses to the high level waste stream (HLW) and to allow recovery of neptunium, the Savannah River Site installed an anion exchange system. The HLW was evaporated and adjusted to about 8M HNO₃ and then fed to the primary recovery column where the anionic complexes of plutonium and neptunium were absorbed. After washing the column with 8M HNO₃, the Pu(IV) and Np(IV) were eluted with dilute HNO₃. After evaporation to concentrate the eluate solution, the solution was fed to a second anion column. After washing, plutonium was partitioned using 5.8M HNO₃, and neptunium eluted with 0.4M HNO₃. The plutonium stream was then transferred to the second plutonium solvent extraction cycle for recovery. The neptunium stream was evaporated and fed to a cation column to absorb the thorium. The neptunium solution was transferred to HB-Line for finishing. [Starks 1977]

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II.A.4.5 Commercial PUREX Processing Plants

28.3.5 UK Thermal Oxide Reprocessing Plant (THORP)

The Thermal Oxide Reprocessing Plant (THORP) in Sellafield, UK is a commercial reprocessing facility that takes irradiated oxide-based fuel from Light Water and U. K. gas-cooled reactors as feed. It separates the uranium and

plutonium from the fission products and produces a vitrified waste product and separate, pure uranium and plutonium oxide streams for re-use as reactor fuel. An aerial view of the plant is shown below:

The plant was designed to process five metric tons per day of fuel irradiated up to 40,000 MWD/tonne and a minimum of five years cooling time. Construction on the plant started in 1985 and first fuel was dissolved in 1994.

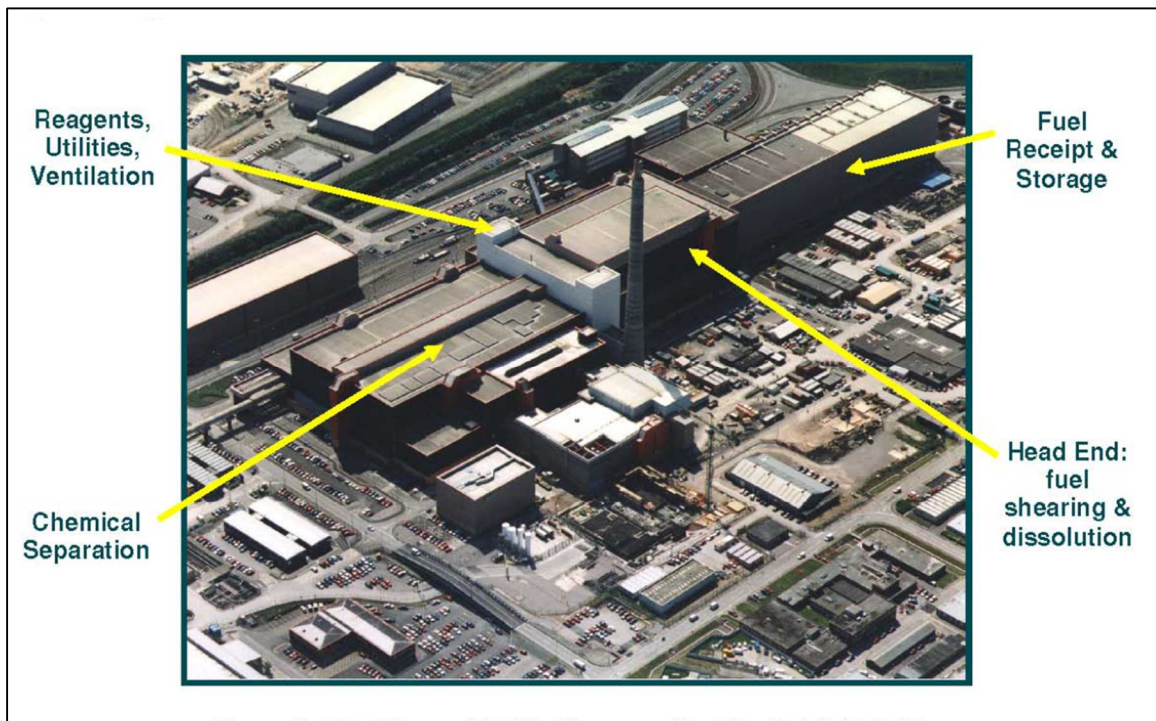


Figure 28.3-5.1 Aerial View of THORP Facility

THORP uses a 'modified' PUREX flowsheet shown below in Figure 28.3-5.2.

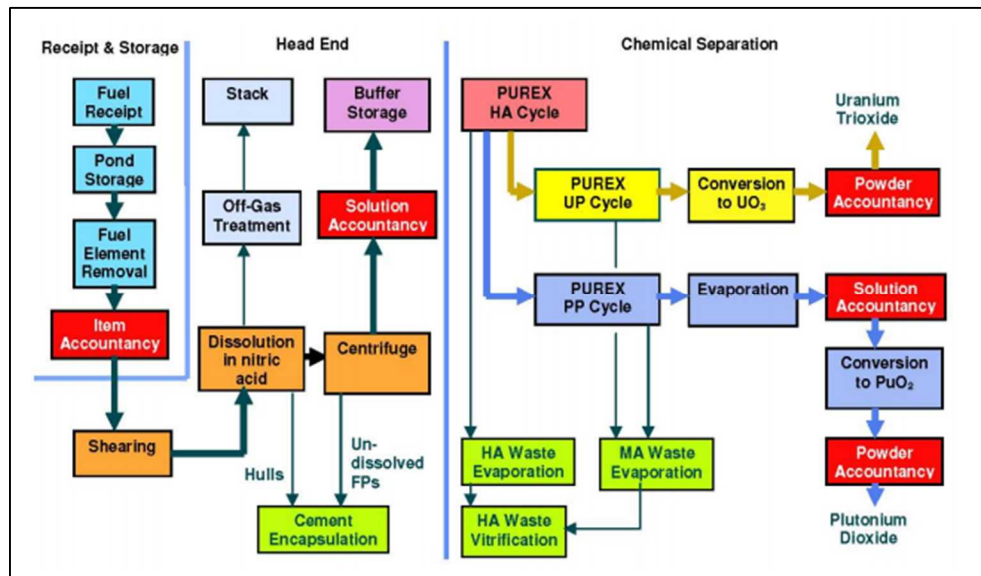


Figure XXX THORP Modified PUREX Flowsheet [Deniss 1990]

In the 'Head End', the fuel elements with either zircaloy or stainless steel cladding are sheared into 5 cm lengths to expose the oxide powder. The sheared fuel is gravity fed into a dissolver with nitric acid to dissolve the oxide and release fission product gases. The fission product gases are scrubbed and the residual gas released. The cladding parts are washed and placed in grout. The flowsheet uses a standard TBP/kerosene solvent in pulsed columns and separates the uranium and plutonium from the fission products in the first high activity (HA) cycle. The raffinate from the HA cycle is sent to evaporation and vitrification which reduces the initial waste volume by 40x. The uranium and plutonium are separated in the second HA cycle by reducing Pu(IV) to Pu(III) using U(IV) as the reductant. U(IV) is considered a 'saltless' reducing agent and does not add any additional 'salts' to the waste stream. Final purification of uranium and plutonium occurred in the UP and PP back-cycles by controlling the chemistry and the oxidation states using hydroxylamine as a 'saltless' reagent. The main contaminants are neptunium and ruthenium. The flowsheet modification is that only one purification cycle is used for both uranium and plutonium instead of two as is used in conventional PUREX flowsheets.

The pure uranium and plutonium nitrate solutions are converted to oxide by thermal denitration and oxalate precipitation respectively. The powders are collected and sent for storage or fuel manufacture.

II.A.4.5.1.1 THORP Plant Performance [Phillips 1991]

All PUREX plants, if operated correctly, can produce very pure uranium and plutonium products with respect to fission products and to each other. Table XXX below shows the decontamination factors of selected fission products from the final UO_3 product.

Table XXX Decontamination Factors (DF) for various fission products and Pu in UO_3 Product

Contaminant	Required DF	Observed DF to U Product
^{99}Tc	4.0×10^3	8.17×10^3 to 2.21×10^5
^{106}Ru	8.7×10^5	4.32×10^6 to 5.91×10^8
$^{134}\text{Cs}/^{137}\text{Cs}$	6.5×10^8	5.66×10^9 to 2.36×10^{10}
$^{144}\text{Ce}/^{144}\text{Eu}/^{145}\text{Eu}$	3.3×10^7	9.36×10^5 to 5.65×10^8
^{237}Np	1.5×10^4	3.31×10^4 to 2.90×10^5
Pu (all isotopes)	5.0×10^6	8.60×10^6 to 1.22×10^{10}

Overall, the single cycle worked well for producing a clean uranium oxide product. Table XXX shows the decontamination factors for selected fission products for the final PuO_2 product.

Table XXX Decontamination Factors (DF) for various fission products and U in Pu nitrate and PuO_2 Product

Contaminant	Required DF	Observed DF to Pu nitrate product	Observed DF to PuO_2 product
All fission products	2.8×10^8	-	3.37×10^8 to 7.06×10^8
^{99}Tc	1.0×10^2	1.00×10^2	-
^{106}Ru	3.2×10^5	1.04×10^6	-
$^{134}\text{Cs}/^{137}\text{Cs}$	5.0×10^6	1.31×10^8	-
$^{144}\text{Ce}/^{144}\text{Eu}/^{145}\text{Eu}$	3.7×10^6	2.10×10^7	-
^{237}Np	4.5×10^1	6.60×10^1	-
Uranium (to nitrate)	4.2×10^3	4.62×10^4	-
Uranium (to PuO_2)	2.1×10^5	-	5.8×10^6 to 5.55×10^8

In addition, the THORP plant demonstrated very low uranium and plutonium losses to the waste streams, typically averaging no more than 0.19% uranium and 0.22% plutonium.

II.A.4.5.1.2 THORP Equipment Design [Phillips 2006]

The design of THORP was a change from the conventional approach of canyons with overhead cranes. Typically, a heavily shielded concrete ‘canyon’ is constructed and a removable ceiling block covers each processing bay. A large overhead shielded crane could remove the block and then access the equipment in the bay. Equipment was designed so that it could be maintained remotely by removing and relocating various piping and equipment parts.

At THORP, the equipment was designed, where possible to have no ‘moving parts’. Airlifts and ‘fluidic’ pump valves and diverters that operate on compressed air were used to minimize maintenance. Where a pump or motor was necessary, the equipment was mounted to use ‘through wall’ drives to allow maintenance in operating galleries without having to enter a high-radioactivity area. Process bays were heavily shielded process cells, called ‘dark cells’ with no routine entry. However, even with this approach, the cells had ‘hatches’ through which cameras could be placed for viewing and where certain equipment, such as in-line filters could be replaced. It also afforded the ability to sample certain points if necessary.

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II.A.4.5.2 French La Hague Reprocessing Plant

La Hague site is an AREVA^{†††††} nuclear fuel reprocessing plant in La Hague on the French Cotentin Peninsula, located 25 kilometers west of Cherbourg, that currently has nearly half of the world's light water reactor spent nuclear fuel reprocessing capacity. The plutonium separation plant UP2 (Usine de Plutonium, or Plutonium Factory) was originally designed to reprocess gas graphite reactor (GGR) spent nuclear fuel at a rate of 800 tonnes per year. Half of the total investment was covered by the military budget, the other half by the civilian budget of the CEA^{#####}. In 1989 a second plant, called UP3 with a nominal capacity of 800 tons was started up at La Hague. It has treated spent nuclear fuel from France, Japan, Germany, Belgium, Switzerland, Italy, Spain and the Netherlands. It extracts plutonium that is then recycled into MOX fuel at the Marcoule site.

The major steps in processing at La Hague are:

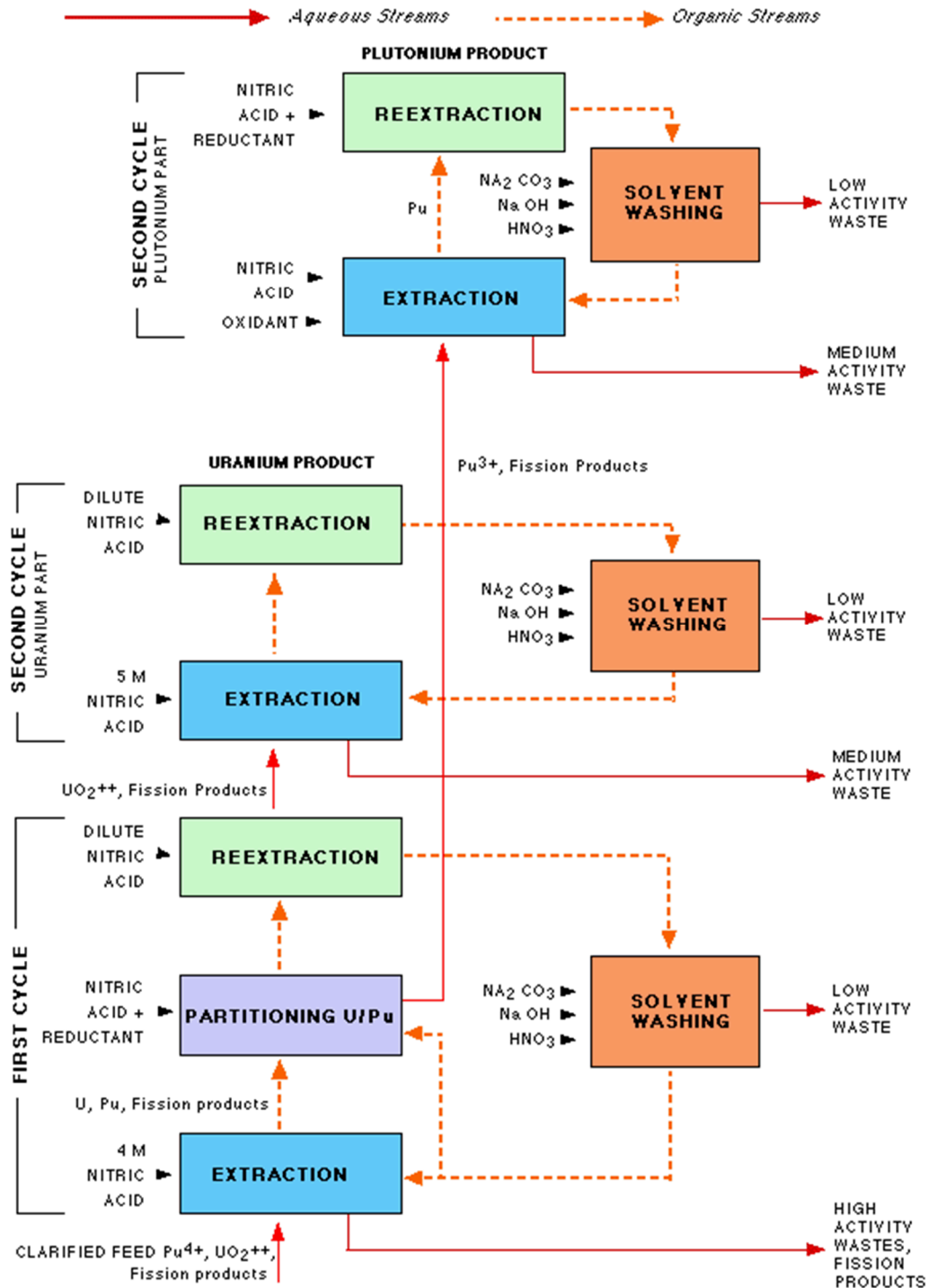
- Receiving and storing fuel prior to processing.
- Separating the various components of spent nuclear fuels and radioactive materials.
- Recovering energy materials (uranium and plutonium) with a view to recycling them in the form of new fuels for the production of electricity.
- Waste conditioning prior to integration into glass for safe, stable conditioning over the very long term, or compacted to reduce their volume.

A typical flowsheet is given in Figure XXXX

^{†††††} The corporate name "Areva" is inspired by the Trappist Santa María la Real monastery in Arévalo in Spain

^{#####} The *Commissariat à l'énergie atomique et aux énergies alternatives* (English: Atomic Energy and Alternative Energies Commission) or **CEA**

REPROCESSING SPENT FUEL: PUREX Flow Sheet



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II.A.4.5.3 Japanese Rokkasho Nuclear Fuel Reprocessing Facility

The Rokkasho Nuclear Fuel Reprocessing Facility (*Rokkasho Kakunenryō Saishori Shisetsu*) is a nuclear reprocessing plant with an annual capacity of 800 tonnes of uranium or 8 tonnes of plutonium. Owned by Japan Nuclear Fuel Limited (JNFL), it is the successor to a smaller reprocessing plant located in Tōkai, Ibaraki in central Japan that ceased operation in 2007. The reprocessing plant is part of the Rokkasho complex located in the village of Rokkasho in northeast Aomori Prefecture, on the Pacific coast of the northernmost part of Japan's main island of Honshu. Construction of the Rokkasho reprocessing plant began in 1993 and was originally expected to be completed by 1997. In June 2013, Areva signed a new strategic agreement with JFNL to bring the Rokkasho recycling plant into commercial operation, including radioactive testing, the start-up itself, capacity ramp-up and plant optimization. Reprocessing activities are now expected to start in March 2016. The plant is not expected to reach its full reprocessing capacity of 800 tonnes uranium per year until 2019. The Rokkasho reprocessing facility is based on the same technology as Areva's La Hague plant in France.

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https://www.iaea.org/INPRO/2nd_Dialogue_Forum/Experience_on_Reprocessing_in_Japan.pdf



The Rokkasho Plant Site (Image: JNFL)

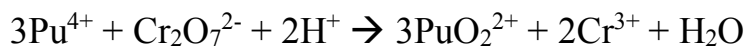
II.B Historically Used Plant Scale Solvent Extraction Processes for Plutonium Recovery

II.B .1 Hexone or REDOX^{§§§§§§} Process

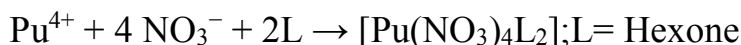
At Hanford, the **REDuction OXidation (REDOX)** processing plant, the first countercurrent, continuous-flow solvent extraction plant in the world, was completed in January 1952; it was the first process to recover both plutonium and uranium. [Gray 2012, DOE/EM 1997, Gerber 1992, Irish 1954, Seaborg 1960, Nash 2006] REDOX used undiluted methyl isobutyl ketone (also known as hexone) as the organic solvent. It is based on the co-extraction of plutonium and uranium in their higher U(VI) and Pu(VI) oxidation states and back extraction of plutonium by selective reduction to the Pu(IV) state. Due to the chemical instability of hexone in even moderately concentrated nitric acid, aluminum nitrate is used as the “salting agent.” It also used tall “packed columns” to achieve contact between the organic and aqueous phases of the process. The extraction is by a *solvation* mechanism. Hexone has a flash point of 60°C, which required all the process equipment to be operated in an inert atmosphere.

^{§§§§§§} REDOX is an acronym that stand for **REDuction OXidation**

REDOX began by decladding and then dissolution of the spent nuclear fuel and targets in nitric acid. The aqueous solution was treated with Na₂Cr₂O₇ to oxidize plutonium to the hexavalent state



Al(NO₃)₃, which was the salting agent, was added under acid-deficient conditions; the solution was then contacted with hexone to extract the plutonium and uranium, leaving the bulk of the fission products, corrosion products, and trivalent actinides in the aqueous phase



Uranium and plutonium were stripped from the hexone phase by water containing small amounts of Na₂Cr₂O₇ (to maintain oxidizing conditions). This cycle was repeated two or three times to get a high DF from the fission products. Finally, the feed solution containing U(VI), Pu(VI), Al(NO₃)₃, HNO₃, and Na₂Cr₂O₇ in the required quantity (for feed adjustment and keeping metal ions as PuO₂⁺² and UO₂⁺²) were contacted with the hexone solution. From the loaded organic phase, plutonium was stripped by an aqueous solution of Al(NO₃)₃ and ferrous sulfamate, which reduces Pu(VI) to Pu(III). Uranium was subsequently stripped with water. To obtain uranium and plutonium in high purity and with high DF from the fission products, the entire cycle was repeated several times.

This process has the disadvantage of requiring the use of a salting-out reagent (aluminum nitrate) to increase the nitrate concentration in the aqueous phase to obtain a reasonable distribution ratio (D value). Hence the process generated enormous volumes of moderately difficult wastes. Also, hexone is degraded by concentrated nitric acid. The process also demanded procedures to accommodate the toxicity and flammability of the extractant. The typical plant-scale performance of the REDOX Process is given in Table XXX.

Table XX Plant-Scale performance of the REDOX Process [Katz 1986]

Separation of uranium from plutonium	> 10 ⁷
Separation of plutonium from uranium	10 ⁶
Decontamination of fission products from plutonium	10 ⁸
Decontamination of fission products from uranium	10 ⁷
Plutonium recovery(%)	99.8
Uranium recovery (%)	99.9

Solvent recovery (%)	92.2
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The REDOX Plant was shut down in December 1967. During its operation, the REDOX Plant processed over 19,000 tonnes of spent fuel. The PUREX process replaced this process: the Hanford Site PUREX plant actually started-up in 1956.

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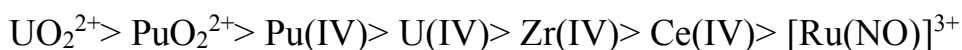
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II.B.2 The BUTEX Process

The basic chemistry of the BUTEX***** Process, first investigated at Chalk River, Ontario, Canada, was the basis of the process at the Windscale Works of the United Kingdom. [Howells 1958, Hinton 1956, Ross 1957, Royston 1973, Shortis 1961] Work was continued at the A.E.R.E. Harwell and the Widnes Research Laboratories of Imperial Chemical Industries Ltd. The process was based on the solvation extraction using the tri-ether extractant β,β' -dibutyoxydiethyl ether, $C_4H_9O-(C_2H_4O)_2-OC_4H_9$. The advantage of the BUTEX Process over the Bismuth Phosphate Process was that uranium and plutonium can be efficiently extracted from a solution of their nitrates while the fission products, with few exceptions, remain virtually inextractable. The BUTEX Process has the advantage over the REDOX Process in that the tri-ether extractant is more stable to nitric acid than hexone and nitric acid could be used, instead of $Al(NO_3)_3$ as the salting-out agent. The BUTEX extractant (dibutyl carbitol) had a higher flash point (hence lower fire hazard) and a low solubility in water. Its primary disadvantages were its high viscosity, its density (near that of water), and the formation of crystalline complexes with uranyl nitrate under certain conditions. The Butex extractant was also decomposed by heating with concentrated nitric acid; however, the extent of decomposition is negligible up to about 20% HNO_3 . At acidities of 50 to 60% HNO_3 the decomposition reaction may become violent with rapid gas evolution. Then Butex extractant and volatile organic degradation products could be effectively removed from aqueous product solutions by steam stripping prior to evaporation. Because of its many disadvantages, the BUTEX Process never came into widespread use.

For the BUTEX Process, the spent nuclear fuel rods were dissolved in 6N nitric acid to produce a uranyl nitrate solution approximately 3N in nitric acid. The distribution coefficients were high enough for efficient extraction at this acidity without the addition of a salt. Over 99.9% of the uranium and 99.98% of the plutonium leaves the column with the solvent phase and 99.5% of the fission product activity remained in the aqueous phase. The fission product activity, which follows the uranium and plutonium, was mainly due to ruthenium with smaller amounts of zirconium, cerium, and niobium.

The following ions are readily extracted into the BUTEX organic phase:



***** **BUTEX** is an acronym that stand for DiBUToxy diethylene glycol (dibutyl carbitol) EXtraction

Plutonium(III) and the remaining fission products transfer into the BUTEX organic phase only to a small extent or are completely inextractable. As with the REDOX and BiPO₄ Processes, neptunium and the transplutonium actinides are rejected to the waste stream in the BUTEX Process. A 3N nitric acid strip was used to remove most of the entrained fission products; this acid concentration was ineffective in stripping ruthenium from the solvent stream containing the uranium and plutonium.

The reducing agent to reduce Pu(IV) and Pu(VI) to Pu(III) was ferrous sulfamate. The ferrous ion and the sulfamate ion act separately. The ferrous/ferric couple reduces the Pu(IV) and Pu(VI) to Pu(III); the sulfamate ion stabilizes the ferrous ion in nitric acid solutions by destroying the nitrous acid that would otherwise oxidize the ferrous ion and so interfere with the reduction of Pu(IV) and Pu(VI) to Pu(III).

The oxidizing agent chosen was dichromate ion. Pu(III) is rapidly and completely oxidized to Pu(IV) and Pu(VI). Ammonium ceric nitrate could have been used but the ceric salt oxidizes the ruthenium to the volatile tetroxide, RuO₄.

The fission product ruthenium forms the complex [Ru(NO)(NO₃)₃], which was easily extracted into the BUTEX organic phase. To minimize contamination of the uranium and plutonium products with the fission product ruthenium, a two solvent extraction process was used. In the plutonium purification process, 20% TBP in odorless kerosene was used as the second solvent. A simplified plant block flow diagram of the process is given in Figure 24.XXX.

Plutonium is stripped from the organic using ammonia to reduce the acidity of the solvent. Ferrous sulfamate was added to reduce Pu(IV) and Pu(VI) to Pu(III) to strip the plutonium into the aqueous phase. The ferrous ion and the sulfamate ion act separately. The ferrous/ferric couple reduced the Pu(IV) and Pu(VI) to Pu(III); the sulfamate ion stabilizes the ferrous ion in nitric acid solutions by destroying the nitrous acid that would otherwise oxidize the ferrous ion and so interfere with the reduction of Pu(IV) and Pu(VI) to Pu(III). An appreciable amount of uranium was stripped along with the plutonium into the aqueous phase.

The further purification of uranium and plutonium are discussed in the next two sections.

Plutonium(III) and the remaining fission products transfer into BUTEX solvent

only to a small extent or are completely inextractable. As with the REDOX and BiPO₄ processes, the BUTEX Process rejected neptunium and the transplutonium actinides to the waste stream.

The plutonium was purified from the residual uranium and fission products and converted to a very pure metal. This process was used at Windscale (now Sellafield) many years ago.

II.B .2.1 Uranium Purification. The solvent containing the uranium was backwashed with dilute nitric acid to strip the uranium. This product was evaporated. Any plutonium is oxidized to Pu(IV) and Pu(VI) during this evaporation step. The concentrate was stored for six months to obtain additional ruthenium decontamination by decay (¹⁰³Ru t_{1/2} = 39.5 d; ¹⁰⁶Ru t_{1/2} = 368 d) before further processing.

The aged uranium solution was adjusted with caustic soda, hydrazine, and ferrous sulfamate. This adjustment reduces the residual plutonium to Pu(III) and modifies the ruthenium species to relatively inextractable forms.

Ammonium nitrate was added to adjust the solution to about 6M nitrate. This salt concentration plus the sodium nitrate present ensures efficient uranium extraction.

The uranium is extracted into the solvent and then backwashed with dilute nitric acid.

II.B.2.2 Plutonium Purification. The BUTEX Process had two plutonium purification cycles. In the first cycle, the Pu(III) and ferrous sulfamate in the aqueous product stream were oxidized with sodium dichromate to mainly Pu(VI), Fe³⁺, and SO₄²⁻. The plutonium was then extracted into the BUTEX Process organic phase and is followed by a wash with dilute nitric acid to strip the plutonium back into the aqueous phase. The plutonium product was concentrated to 2-3 g/L Pu for feeding to the second plutonium purification cycle.

For the second plutonium purification cycle, the plutonium was completely converted to Pu(IV) by the following steps.

- A. Acidity was adjusted to 8.4N nitric acid
- B. Hydrazine nitrate was added and the temperature was maintained at 90° C for 30 minutes. Reduction to Pu(III) is rapid.

- C. As the hydrazine was destroyed by the nitric acid, re-oxidation of the plutonium to Pu(IV) occurs.
- D. To complete the oxidation, the solution was cooled to 20° C and sodium nitrite was added. This addition destroyed the residual hydrazine.

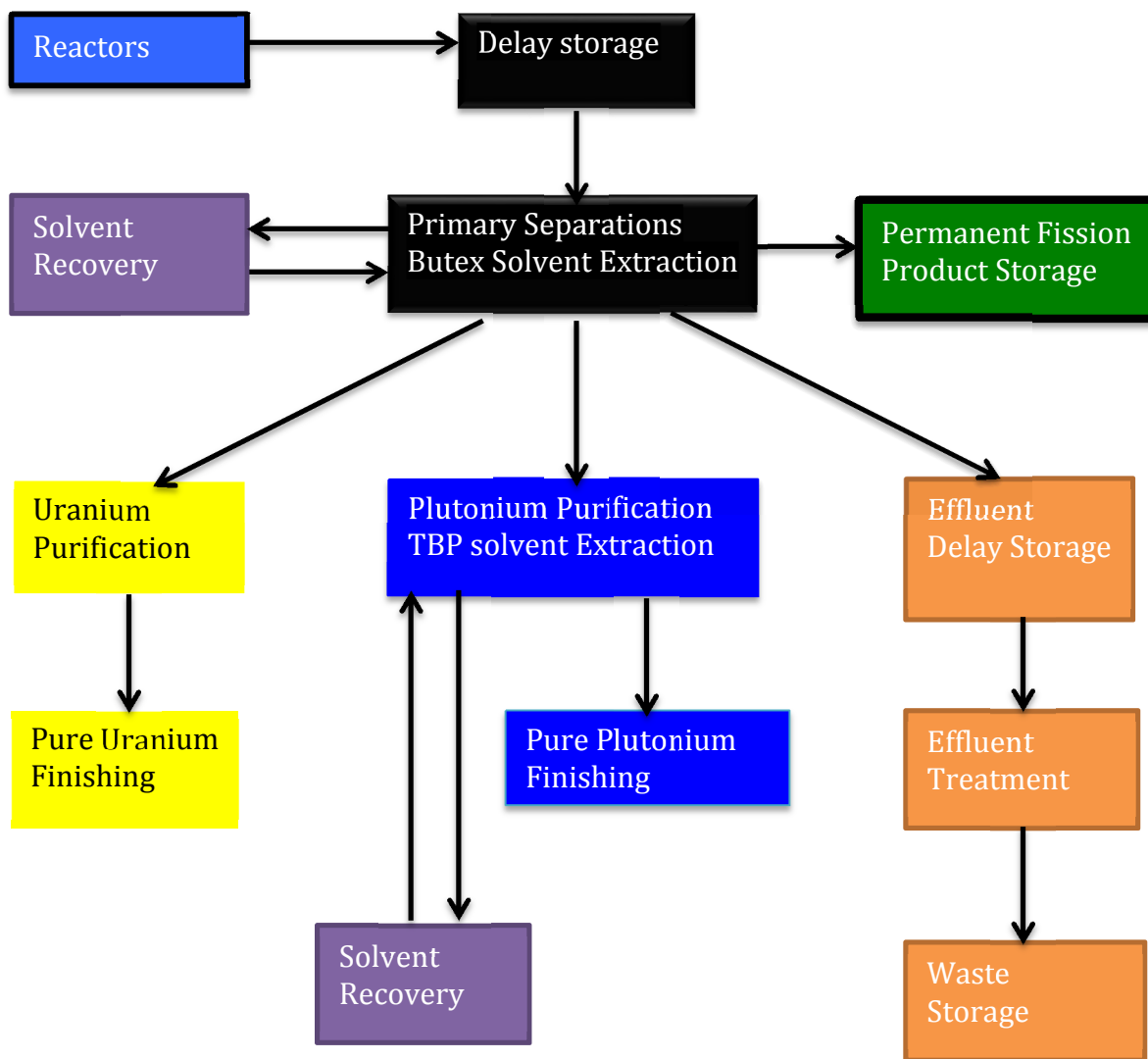
The adjusted feed is then fed to a TBP solvent extraction cycle. The use of 20% TBP diluted in oleum washed kerosene in the second plutonium purification cycle results in a much higher decontamination from ruthenium than with the BUTEX extractant. The residual ruthenium and zirconium are stripped from the organic phase using 3N nitric acid. Plutonium is then stripped from the organic phase using 0.25N nitric acid.

II.B .2.3 BUTEX Contactors. The Windscale Works use a combination of six contactors/extractors in the BUTEX Process. These were:

- A. Simple stirred pot and separator,
- B. Holly Mott type (gravity-flow mixer-settlers) vessels, with recirculation of the aqueous phase in the Solvent Washing unit operations,
- C. Vertical columns packed with Lessing Rings in the Primary Separation Process,
- D. Vertical Pulsed columns packed with Lessing Rings in the Plutonium Purification Section,
- E. Air Lift extractor,
- F. Mechanically stirred (pump-mix) Mixer Settler in the Uranium Purification Process.

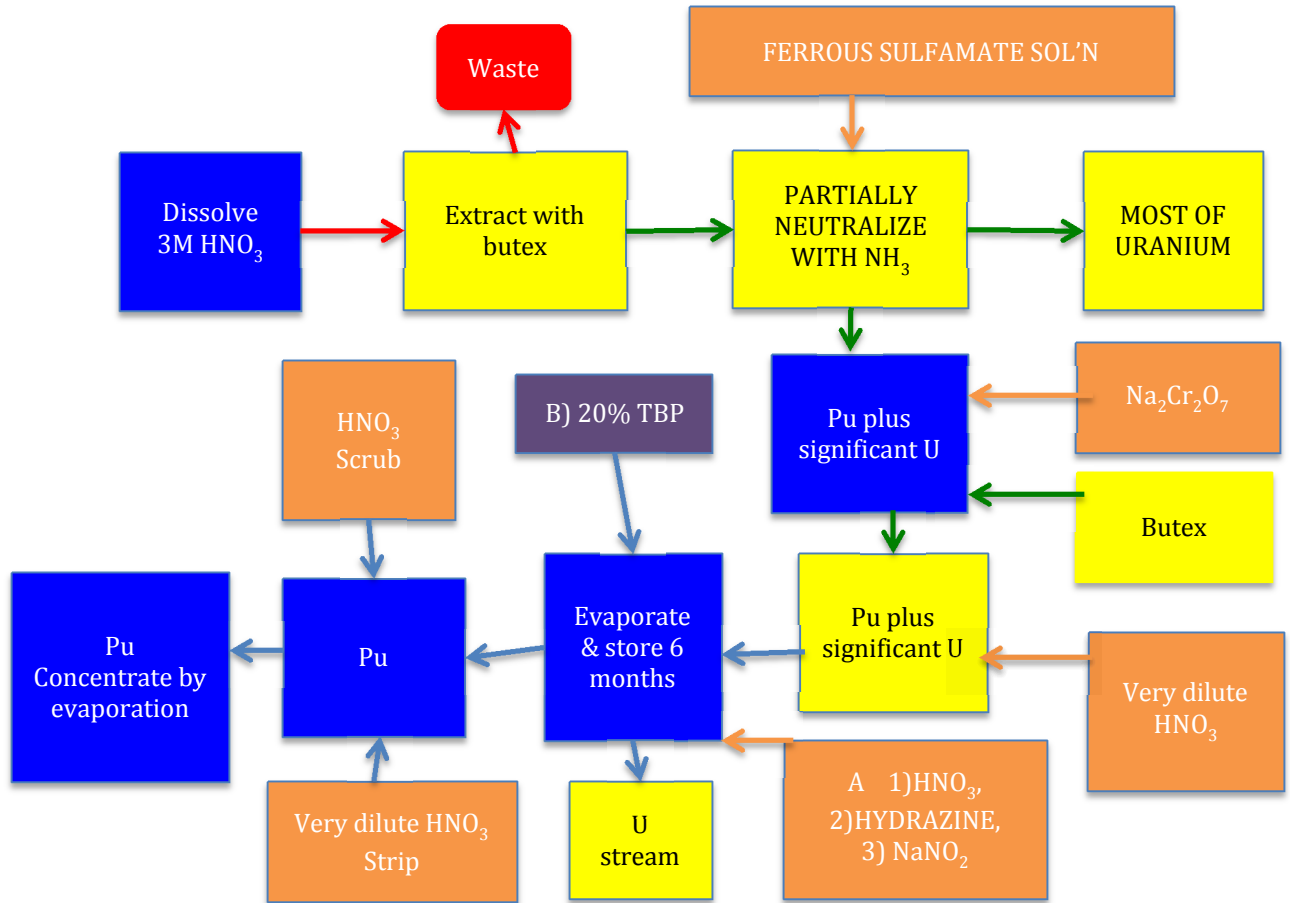
The BUTEX Process has been replaced by the PUREX Process.

Figure XXX. Simplified BUTEX Flowsheet^{†††††††}



††††††† See Figure XXX for the Primary Separations Butex Solvent Extraction Flowsheet.

Figure.XXX Primary Separations BUTEX Solvent Extraction Flowsheet



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II.C Historically Used Precipitation Processes for Separations of Plutonium and Uranium

Two precipitation processes have been used to separate and purify plutonium and uranium. These are

1. The Bismuth Phosphate Process
2. The Uranyl Acetate Process

II.C.1 The Bismuth Phosphate Process

The first large-scale nuclear reactors were built during World War II. These reactors were designed for the production of plutonium for use in weapons programs.***** The only reprocessing required, therefore, was the extraction of the plutonium (free of fission-product contamination) from the spent natural uranium fuel. In 1943, several methods were proposed for separating the relatively small quantity of plutonium from the uranium and fission products.

***** Within the context of world politics in the 1930s and 1940s, it was inevitable that the discovery of fission would be first valued for its potential military applications. Two approaches to the assembly of a critical mass were immediately recognized: isotope enrichment to increase the atom percentage of the fissile uranium isotope ^{235}U and transmutation of ^{238}U by neutron capture and β^- decay to produce ^{239}Pu and chemical separation from different elements. Differences in the redox chemistries of uranium and plutonium facilitate their mutual separation.

The isolation of plutonium from uranium and fission products was initially accomplished by co-precipitation with BiPO_4 . §§§§§§ The process, pioneered by S. G. Thompson [Thompson and Seaborg, 1956, 1957; Seaborg and Thompson, 1960], involves co-precipitation of Pu(IV) by BiPO_4 followed by oxidation to Pu(VI), which does not carry on BiPO_4 , i.e. the “Bismuth Phosphate Process.” This method was further developed and tested at the Oak Ridge National Laboratory (ORNL) between 1943 and 1945 to produce gram quantities of plutonium for evaluation and use in the U. S. weapons programs. ORNL produced the first gram quantities of separated plutonium with these processes. [DOE/EM 1997, Cleveland 1980, Thompson and Seaborg 1957a, Thompson and Seaborg 1957b, DOE/EM-0319 1997. Gray 1999, Long 1978]

The Bismuth Phosphate Process was first operated on a large scale at the Hanford Site on the Columbia River near Richland, Washington, in the latter part of 1944. It was successful for plutonium separation in the emergency situation existing then, but it had a significant weakness: the inability to recover uranium. The Bismuth Phosphate Process, while effective, was inefficient, processing only 1 to 1.5 tons of fuel per day, whose plutonium content was approximately 300 ppm.

The Bismuth Phosphate Process separated and purified plutonium through successive cycles of precipitation and dissolution using bismuth phosphate as the carrier. This batch process was based on the fact that plutonium will co-precipitate with bismuth phosphate in the Pu(IV) valence state, but not in the Pu(VI) valence state. The aluminum cladding around the uranium was dissolved in boiling NaOH and removed to waste. Bismuth phosphate was dissolved in concentrated nitric acid using a mercury catalyst along with the irradiated uranium; plutonium was separated and concentrated by many cycles of precipitation and dissolution using bismuth phosphate. Changing the chemistry of the solution caused bismuth phosphate to solidify into a fine, powdery precipitate. In each byproduct precipitation, wastes and impurities were solidified with the bismuth phosphate while the plutonium remained dissolved. The waste precipitate was removed from the solution in a centrifuge. The cake of solid waste left in the centrifuge was dissolved and transferred to the waste tanks, while the liquid went to the next step. Following each byproduct precipitation was a product precipitation. Changing the chemistry of the solution

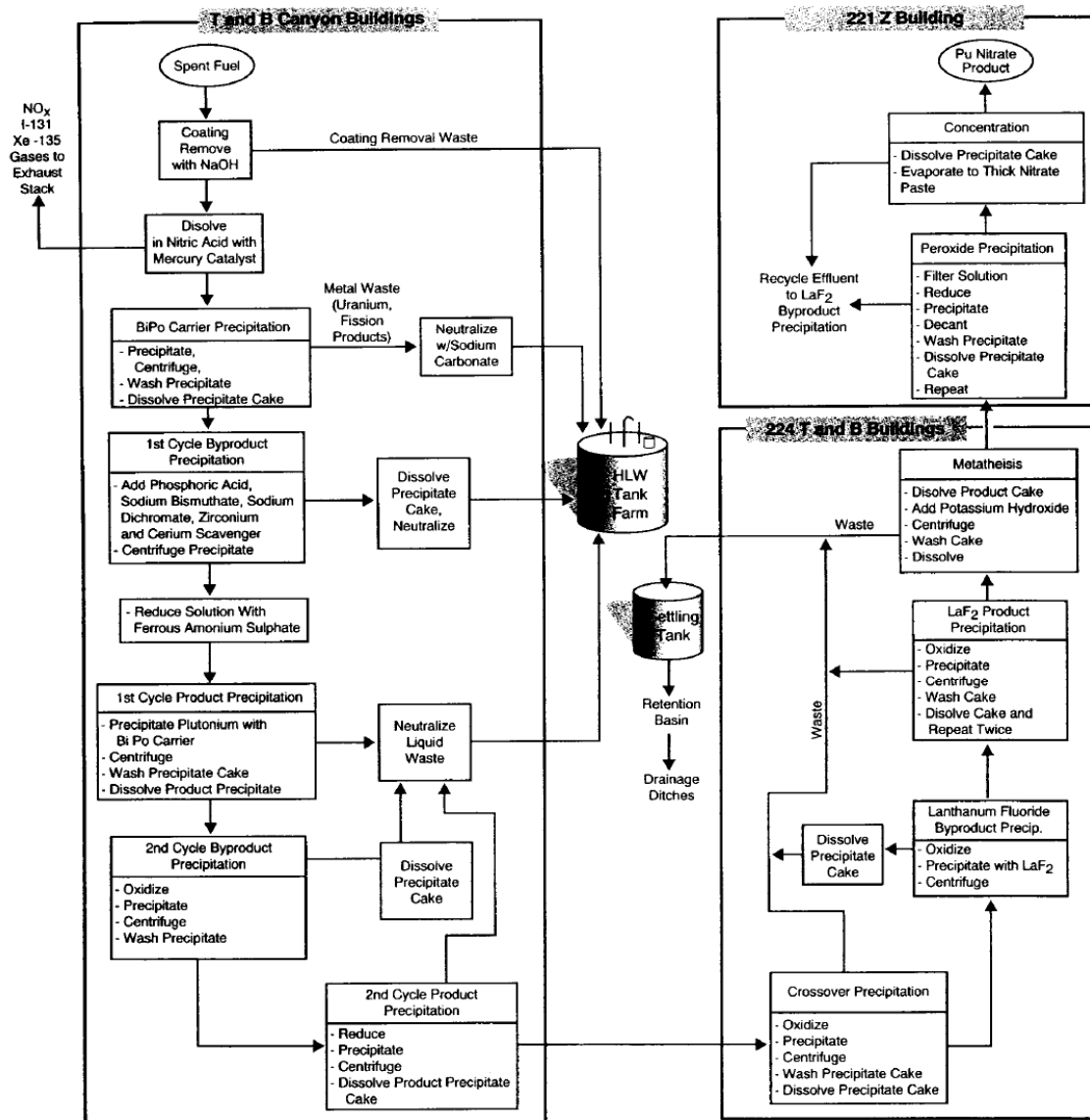
§§§§§§ A historical perspective on the development of this science and technology through the end of World War II is available in “The Making of the Atomic Bomb.” [Rhodes 1986].

allowed plutonium to be carried out of the solution with the bismuth phosphate precipitate, so that it could be separated from the impurities that were not removed with the bismuth phosphate. After centrifuging out the waste liquid, the cake of bismuth phosphate and plutonium was redissolved and sent on for further purification and concentration. Lanthanum fluoride replaced bismuth phosphate in the final concentration and purification, using a similar process. See Figure XXX for a schematic of the process.

The bismuth phosphate process could only extract plutonium; the uranium remained in the high-level waste stream. After the war, additional separations of BiPO_4 wastes were conducted to recover the rejected uranium for recycle to reactors.

Figure XXX. Bismuth Phosphate Chemical Separations at Hanford [DOE/EM 1997]

Figure B-12. Bismuth Phosphate Chemical Separation at Hanford



Note: The bismuth phosphate process separated and purified plutonium through successive cycles of precipitation and dissolution using bismuth phosphate as a carrier. Bismuth phosphate was dissolved along with the irradiated uranium. Changing the chemistry of the solution caused bismuth phosphate to solidify into a fine, powdery precipitate. In each byproduct precipitation, wastes and impurities were solidified with the bismuth phosphate while the plutonium remained dissolved. The waste precipitate was removed from the solution in a centrifuge. The cake of solid waste left in the centrifuge was dissolved and transferred to the waste tanks, while the liquid went on to the next step. Following each byproduct precipitation was a product precipitation. Changing the chemistry of the solution allowed plutonium to be carried out of the solution with the bismuth phosphate precipitate, so that it could be separated from impurities that were not removed with the bismuth phosphate. After centrifuging out the waste liquid, the cake of bismuth phosphate and plutonium was redissolved and sent on for further purification and concentration. Lanthanum fluoride replaced bismuth phosphate in the final concentration and purification, using a similar process.

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II.C.2 Sodium Uranyl Acetate Process

The bases of the sodium uranyl acetate procedure was first worked out at the University of California at Berkeley and used to isolate the first 1.2 mg of plutonium (^{239}Pu) from one tonne of uranium as uranyl nitrate. Los Alamos

National Laboratory re-examined the procedure in 1950 as a method for separating iron from plutonium [Mullins, 1950]. The Russians scaled up this procedure and used it in all three of their separations plants. [Gray1993, Wick 1967, Cleveland 1980, Hamaker 1943, Golfman 1995, Cleveland 1970, Cleveland 1979, Gray 1999, Katz 1986, Pittman 1950]

SIDEBAR

First isolation of a milligram of Plutonium

John Gofman discussed his work on the chemistry of plutonium.:

Thinking “that plutonium in the higher oxidation state would behave like uranium...” and knowing about sodium uranyl acetate he thought “...that plutonium might behave that way.” He “tested that and it did behave that way.”

“If you precipitated sodium uranyl acetate, even if you had a limited number of atoms of plutonium, the plutonium went with the sodium uranyl acetate...I worked out a process that would isolate plutonium away from uranium and then get it back with uranium. I could cycle it back and forth to get rid of the fission products...On a lab-bench scale ...it all worked fine and the plutonium came through the process.”

Oppenheimer needed a half a milligram of plutonium “but there was only a twentieth of a milligram in existence...we got the ton of uranium nitrate stacked around the Berkeley cyclotron to capture every neutron that was escaping. Bombarded it for about 6 to 7 weeks. Let it cool a little... we set up big jars and handled 10 pounds of uranium at the time. With each jar, we took it the first step of the process and then the second step.”

“After about three weeks of around-the-clock work, we had it down to about a quarter-teaspoon of liquid with plutonium in it and nothing else. We had 1.2 milligrams, and we just needed a half-milligram.”

The uranyl and plutonyl ions both form complexes with acetate ions. Bonding is through both oxygen atoms of the carbonyl group to the central MO_2^{2+} ions. The

acetate complexes owe their importance to the selective reactivity of the acetate ion with respect to the Ac(VI) , MO_2^{2+} , ions. Sodium, potassium and guanidinium (aminomethanamide, CH_5N_2) acetates form comparatively insoluble complexes with the uranyl ions, thus offering the possibility of separating uranium from many impurities. The sodium salts, $\text{NaMO}_2(\text{CH}_3\text{COO})_3$ (where $\text{M} = \text{U, Np, Pu, or Am}$) are isomorphous.

Sodium plutonyl acetate is pink compound, has a cubic structure, and a calculated density of 2.578 g/cm^3 .

The solubility of sodium uranyl acetate in a 5M NaNO_3 - $1\text{M CH}_3\text{COOH}$ - $0.5\text{M Na}(\text{CH}_3\text{COO})$ solution is about 100 mg/L . Neptunium(VI) and plutonium(VI) also precipitate under these conditions. The solubility of $\text{NaPuO}_2(\text{CH}_3\text{COO})$ in water varies from 6 g/L at 5°C to 19 g/L at 95°C . The solubility of plutonyl acetate in $0.6\text{M CH}_3\text{COOH}$ - $0.2\text{M Na}(\text{CH}_3\text{COO})$ solutions containing various concentrations of NaNO_3 , expressed as grams of plutonium per liter, decreases from 1.0 for 0.8M NaNO_3 to 0.07 for a 5.7M NaNO_3 solution.

Pure sodium plutonyl acetate may be prepared by addition of sodium acetate and sodium nitrate to a solution of Pu(VI) in 0.2M HNO_3 - 0.9M acetic acid- 0.1M sodium dichromate such that the final solution is 5M in sodium ion, 0.6M in acetic acid, and 0.2M in acetate ion. This slow precipitation requires about two hours.

The steps in the sodium uranyl acetate precipitation process for spent fuel reprocessing are:

1. The uranium fuel is dissolved in a solution yielding about 1 to 2M HNO_3 .
2. The plutonium valence is adjusted to Pu(VI) by the addition of sodium dichromate. The valence adjustment is important as Pu(VI) is carried with the uranium, but Pu(IV/III) remains in solution. This behavior of the different plutonium valence states is basis for the initial separation from fission products from uranium and plutonium.
3. The solution is adjusted to a near neutral solution of about 5M NaNO_3 - $1\text{M CH}_3\text{COOH}$ - $0.5\text{M Na}(\text{CH}_3\text{COO})$. The uranium and plutonium are allowed to co-precipitate. This precipitation is a slow process requiring several hours.
4. After the precipitate has settled in conical tanks, the bulk of the solution, containing the bulk of the fission products, is then decanted. The resulting HLW solution is a concentrated salt solution, having a NaNO_3

concentration > 100 g/l and a $\text{Na}(\text{CH}_3\text{COO})$ concentration of 60-80 g/l. The high salt concentration restricts the degree of volume reduction and makes overall waste volumes higher. [Cochran 1995]

5. The slurry is washed with a similar solution and again decanted to remove more fission products.
6. The precipitate is dissolved in nitric acid and the precipitation repeated as many times as necessary to sufficiently decontaminate the uranium/plutonium product of fission products.
7. The product slurry is again dissolved in nitric acid, the plutonium valence adjusted to Pu(III). Then the uranium is precipitated as above.
8. After the solids have settled, the solution containing the bulk of the plutonium is decanted away.
9. The slurry is wash with a similar solution and again decanted.
10. The plutonium can now be concentrated by adding back a small amount of uranium and precipitating as above.
11. By adjusting the valence of plutonium to Pu(III) the uranium can be precipitated leaving a pure plutonium solution.

There were difficulties with the acetate process. For example, in the last decontamination stage, which had to be supplemented with a lanthanum fluoride carrier precipitation process to get the purity required, the equipment had to be coated with gold or silver to resist corrosion. [Cochran 1995] In addition, the large HLW volumes with high concentrations of acetate were a problem for storage and handling. To overcome this, a technique was developed for concentrating the waste. First, the fission products were concentrated by co-precipitation with iron and chromium hydroxides, iron and nickel sulfides and nickel ferrocyanide. The resulting suspension was clarified; the fission products removed for long-term storage and the decanted solution was acidified with nitric acid. Then, the solution was evaporated and the acetic acid was removed as a distillate in a plate column and the bottoms were crystallized sodium nitrate. [Cochran 1995]

II.C .2.1 Using Basic Acetate Precipitation to Separate Iron from Plutonium

Based on earlier results using acetate-based precipitations for plutonium recovery, the 'basic acetate' precipitation process was examined as a method to separate iron from plutonium [Mullins, 1950]. The plutonium was oxidized with KMnO_4 to Pu(VI) and the iron was precipitated with ammonium acetate. The following results were reported. Between 96% to 98% of the plutonium was separated from iron when the acetate concentration is $> 1.9\text{M}$ and the plutonium

is completely oxidized to the Pu(VI). The Pu(VI) carried by the precipitate is primarily a function of the acetate concentration and is not affected by initial iron concentrations from 0.005 M up to 0.1 M Fe. U(VI) is an effective 'holdback' carrier, keeping the Pu(VI) in solution when plutonium is present in tracer quantities. However, the effect is negligible for macro quantities of Pu. The final conclusion was that 'basic acetate' precipitation was not effective for iron- plutonium separations and would not be further developed for plant operations.

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II.D Concentration Procedures

Basically three processes have been used to concentrate the purified plutonium stream:

1. Evaporation
2. Cation Exchange
3. Anion Exchange

II.D.1 Evaporation

For the evaporation step, the product from solvent extraction typically is evaporated from the range of 1 to 20 g of Pu/L to about 350 to 400 g of Pu/L; evaporation eliminates a large portion of the water and the excess nitric acid. However, all of the impurities in the solvent-extraction product are also concentrated.

II.D.2 Ion Exchange Processes

The development of solid materials capable of capturing and reversibly releasing the metal ions back into the contacting solution, ion exchange materials, was a great step forward in separating elements with similar properties. [Nash 2006]

Both cation and anion exchange can be used to further separate plutonium from fission products, uranium, neptunium, and other impurities as well as to concentrate the plutonium for downstream processing. [ORNL 1961, James 1966, Wick 1967, Cleveland 1980, Gray 2012, Cleveland 1970, Cleveland 1979, Gray 1999, Long 1978, Logsdail 1985, Navratil 1989] Of the two processes, anion exchange is more efficient at decontaminating solutions that are high in impurity salts or that contain concentrated acids. Cation exchange is more efficient when dealing with large volumes of dilute plutonium solutions containing low-concentration of acid and salts. Table XXX lists the decontamination factors for plutonium from various elements. [Katz 1986, Cleveland 1980, Gray 2012]

Table XXX. Decontamination Factors for Plutonium

Element	Cation Exchange	Anion Exchange
Ag		<50,000
Al		>7,700
Ca	>20	>20,000
Cr		20,000
Cu		10,000
Co		
Ce		
Fe		44,000
K	>30	>20,000
Li		>100,000
Mg	>25	5,000
Mo		
Na	>100	500
Nb	<10	
Ni		>10,000
Ru	2 to 4	
Ce		
U	4 to 900	
Zr	<10	

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II.D.2.1 Cation Exchange

During the Manhattan Project, ion exchange was considered an alternative to the bismuth phosphate precipitation flow sheet used at Hanford. However, the cation-exchange process was not adopted because of the low decontamination factors.

Cation exchange is used primarily to concentrate and recover plutonium from the dilute PUREX process product streams. [Wick 1967, Cleveland 1980, Gray 2012, Cleveland 1970, Cleveland 1979, Gray 1999, Orth 1961a, Orth 1961b, Moore et al. 2000, TID 1961, Ryan and Wheelwright 1959, Long 1978] At the Oak Ridge National Laboratory, Overholt, Tober, Orth, etc. [Overholt et al.] developed the cation exchange operations for the Savannah River Site. At the Savannah River Site [Orth 1961a, Bonner 1956], the PUREX product solution contained the holding reductant hydroxylamine, which was added to aid in stripping plutonium from the solvent, and was processed directly with no further feed adjustment. The system handled large volumes of dilute feed efficiently; on occasions, solutions with plutonium concentrations as low as 0.001 g of Pu/L were processed without difficulty. Some of the advantages of the cation-exchange process were:

- Losses were sufficiently low that recycle or recovery of the column waste was unnecessary.
- Capability of concentrating the PUREX product stream fifty-fold or more.
- Provided additional decontamination for uranium, fission products, and anionic impurities.
- No requirement for high temperature or pressure.
- No mechanism for formation of explosive compounds from entrained organic solvent.
- Ability to maintain plutonium as the Pu (II) species, which proved to be favorable for downstream processing.

The cation-exchange process was used at Savannah River for approximately 50 years; the basic process remained virtually unchanged.

The resin used at the Savannah River Site was Dowex 50, polystyrene divinylbenzene beads with exchange sites that were strongly ionized sulfonic acid groups. The plutonium cations [as Pu(III)] exchanged with the hydrogen ions during absorption in weak nitric acid solution, and were removed during elution with moderate strength nitric acid solution. The optimum resin size, 50 to 100-mesh, was a compromise between capacity and absorption rates versus bed pressure drop.

For criticality safety, the Savannah River Site operated two columns (separated adequately for criticality safety) in series to serve as a single unit; the effective resin depth was 10 inches. The units operated with down-flow loading and wash cycles^{*****} and up-flow elution and reconditioning cycles.

For the Savannah River Site operations, selecting an anion-exchange system to concentrate the PUREX product solution would have had several disadvantages:

- The already large feed volumes would have to been doubled for acid adjustment.
- Nitrite would have to be added for valence adjustment.
- The columns would have required operation at elevated temperatures for reasonable exchange rates to be achieved.
- The same unit throughput would have required either more equipment or faster flow rates, with attendant higher feed pressures on the hot, strong nitric acid solutions.
- The higher losses would have required plutonium recovery from the waste or much longer columns (with attendant higher feed pressures) be used.
- For economic reasons, the large amount of nitric acid would require recovery from the waste stream.

For the cation-exchange concentration, the plutonium remains in a reducing solution as Pu(III). As the Pu(III) loads the cation-exchange resin, all elements in the M^{+1} and M^{+2} oxidation state are partly forced off the resin to the waste stream by the loading Pu(III). Therefore the solution is further decontaminated

***** Anions and most of the monovalent and divalent cationic impurities report to the effluent stream during loading operations. If required, additional uranium and fission products can be removed using a dilute sulfuric acid wash.

(from Fe^{2+} , Ni^{2+} , UO_2^{2+} , ZrO_2^{2+} , NbO_2^{2+} , RuO_2^{2+} , Na^+ , etc.) instead of the impurities being concentrated along with the plutonium.^{††††††††} The primary disadvantage of cation exchange is the limited Decontamination Factor (DF) for fission products. A major benefit of the cation-exchange system at the Savannah River Site was that the PUREX product solution was already properly adjusted for the cation-exchange operation and no dilution of the solution for valence and acid adjustment was necessary. However, at the Savannah River site a small volume of ascorbic acid was added to ensure that all the plutonium was Pu(III) when fed to the column. The main benefit is the increase in plutonium concentration from very dilute solutions to about 30 to 60 g of Pu/L (hearts cut). At Savannah River the typical concentration of cation exchange product solution was about 30 g of Pu/L. Losses were sufficiently low that recycle of the cation column raffinate was unnecessary.

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^{††††††††} Additional decontamination can be obtained by washing the column with a dilute sulfuric acid-hydroxylamine solution. The sulfuric acid forms sulfate anion complexes with some of the cationic impurities, allowing them to be removed from the system.

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II.D.2.2 Anion Exchange

Anion exchange is extremely valuable when plutonium must be recovered and decontaminated from concentrated acid and salt solutions. [Wick 1967, Cleveland 1980, Ryan 1960, Gray 2012, Cleveland 1970, Cleveland 1979, Gray 1999, Orth 1961a, Orth 1961b, Moore et al. 2000, TID 1961, Katz 1986, Silva 1984, Long 1978, Ryan 1961, Swift 1961, Wheelwright 1962, Ryan 1959, Kaya 1966, Bradley1997] In the anion-exchange process, plutonium is adsorbed onto an anion exchange resin from a strong nitric acid solution and eluted with dilute nitric acid.

In strong nitric acid solutions, Pu(IV) forms a hexanitrate anionic complex, $[\text{Pu}(\text{NO}_3)_6]^{2-}$. Ryan [Ryan 1960 and Cleveland 1979] reports the following abundances of the hexanitrate complex as a function of nitric acid concentration:

Table XX Abundance of Pu(IV) hexanitrate complex in HNO_3 solutions

HNO_3 , M	% Abundance of $[\text{Pu}(\text{NO}_3)_6]^{2-}$
5	4
6	10
7	29
8	50
9	75
10	91
11	95
13	100

The hexanitrate complex strongly adsorbs on the anion resin. The maximum distribution coefficient for Pu(IV) is obtained from solutions containing about 7-8 M nitric acid. The Los Alamos National Laboratory used 7.0 to 7.5M and the Savannah River Site used 7.5 to 8.0M with good results. Use of acidities as high as 10M is possible. The distribution coefficient is reduced as the acidity is raised due to the protonation of the di-anionic hexanitrate ion, $[\text{Pu}(\text{NO}_3)_6]^{2-}$.

Pu(IV) adsorption is more strongly influenced by kinetics, (which demands higher temperatures) than by equilibrium (which is an exothermic reaction and requires lower temperatures). The large size of the plutonium hexanitrate complex presumably causes the ion exchange rate to be slow.

After loading, the resin is usually washed with 6-7 M nitric acid to remove weakly adsorbed impurities. Plutonium is then eluted from the resin with dilute nitric acid because the anionic plutonium hexanitrate complex decomposes in dilute nitrate solutions. Usually 0.35 M nitric acid is used; lower acid concentrations are avoided to prevent hydrolysis and plutonium polymer formation.

The anion-exchange process offers excellent product decontamination since few metal ions form anions in 6-7 M nitric acid. Np(IV) and Th(IV) also form hexanitrate complexes, which can load onto the resin. Use of a small amount of fluoride ion in the wash, however, improves the decontamination. Since most elements do not form nitrate anionic complexes, the distribution ratio of these elements adsorbed onto anion resin from 1-14 M nitric acid is very low. The elements that show weak adsorption can be easily washed from the column with one or two bed volumes. Elements such as Hg(I), Ce(III), U(VI), and Bi(III) require more wash solution. The strongly adsorbed platinum group metals can be separated from plutonium because they do not elute with dilute nitric acid. Thus with nitric acid conditions, the two most difficult ions to separate from plutonium via anion exchange is Np(IV) and Th(IV). With proper valence control, anion-exchange was used to remove neptunium in recovering ^{238}Pu from irradiated neptunium at the Savannah River Site. [Burney 1964, Groh 1970]

Three classes of ion-exchange equipment have been developed for use in spent nuclear fuel reprocessing: (1) fixed beds, (2) moving beds, and (3) expanded or fluidized beds. Fixed and moving beds were the most widely used. [Long1978]

For several years Hanford routinely used anion exchange to replace the third cycle of solvent-extraction plutonium purification. Hanford used moving-bed ion-exchange equipment known as a Higgins contactor. The resin flow was not truly continuous. Batches of loaded resin are periodically transported from the sorption stage to the desorption stage, and equal batches of stripped resin were returned to the sorption stage. The batches are small enough and the resin movement was frequent enough that the practical behavior is the same as if resin movement were continuous. [Long 1978]

The Hanford Site, the Savannah River Site and Mayak^{*****} plant in Russia used fixed bed anion exchange to separate ^{238}Pu and ^{237}Np for the production of ^{238}Pu heat sources. The Savannah River Site also used anion exchange for recovering and purifying plutonium from miscellaneous solutions and solids generated during production of plutonium metal from the cation-exchange system. [Ryan 1959, Bradley 1997]

Anion-exchange resins give excellent decontamination from the concentrated salt solutions. Table XXX above lists decontamination factors (DF) for plutonium by element. [Katz 1986, Orth 1961a, Silva 1984, Wick 1980]

For anion-exchange concentration, the plutonium must be oxidized from the Pu(III) to the Pu(IV) state and the nitric acid concentration increased to approximately 7 M. (For the PUREX product solution, the volume had to be approximately doubled to make this adjustment.) This adjustment results in the formation of the plutonium nitrate complex anion, $[\text{Pu}(\text{NO}_3)_6]^{2-}$. All elements not forming at least a neutral complex with nitrate ion are not collected by the anion resin, hence are rejected to the waste stream.^{§§§§§§§§} Plutonium was collected on the anion resin as the anion $[\text{Pu}(\text{NO}_3)_6]^{2-}$. As with the cation exchange operation used at the Savannah River Site, the solution was further decontaminated (from Fe^{3+} , Ni^{2+} , Na^+ , etc.) instead of these impurities being concentrated along with the plutonium, as was done with an evaporation operation.

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^{*****} The Mayak Production Association; Mayak translates to English as "lighthouse". Mayak was formerly known as Chelyabinsk-40 and later as Chelyabinsk-65, referring to the postal codes of the site.

^{§§§§§§§§} The $[\text{Pu}(\text{NO}_3)_6]^{2-}$ complex ion forms in high nitric acid concentrations, and it is very strongly held by anion resin. Other tetravalent actinides, e.g., neptunium, form similar complex ions. The hexavalent metals (i.e., UO_2^{+}) form considerably weaker complexes, and the trivalent and pentavalent species are complexed to a very small extent. With the exception of Ru, Tc, and Ce(IV), fission products do not form such complexes and are only weakly held by the resin. As a result, very high DFs can be obtained for the plutonium. In dilute nitric acid (0.5N), the plutonium hexanitrate complex ion is not stable, so plutonium can be eluted from the resin.

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II.E Isolation Processes

A variety of processes can be used to convert plutonium to a solid form of either metal or oxide (PuO_2), typically referred to as plutonium oxide. [Wick 1967, Cleveland 1980, Gray 2012, Cleveland 1970, Cleveland 1979, Gray 1999, Long 1978] The major methods are direct precipitation of the Pu(IV) with hydrogen peroxide, or precipitation of either Pu(III) or Pu(IV) with oxalic acid^{*****}. The

^{*****} Either oxidation state of plutonium can be precipitated by adding oxalic acid to the plutonium solution or by adding the plutonium to the oxalic acid.

Pu(III) oxalate precipitation is easiest to control and still yields an easily filterable product. Precipitation of Pu(IV) with either hydrogen peroxide or oxalic acid gives better decontamination from residual impurities but both require very close control of the precipitation parameters. It is possible to precipitate Pu(III) as a fluoride, but the product is only suitable for metal production. The final method is to concentrate the solution and then direct calcination or denitration to produce PuO₂. This method introduced problems (e.g., mastic phase operations) when attempting to de-nitrate plutonium nitrate solutions. The Japanese overcame these problems by first blending the plutonium nitrate with uranium nitrate prior to denitration of the combined solution.

Plutonium finishing at the major commercial reprocessing facilities in the United Kingdom and France is based on the precipitation of Pu(IV) oxalate from the Pu(III) nitrate product of the PUREX Process. After blending of nitrate solutions to ensure a homogeneous batch with respect to concentration, isotopics, and impurities, the solution is conditioned with hydrogen peroxide solution to adjust the plutonium to the Pu(IV) oxidation state. Precipitation of either Pu(III) or Pu(IV) is possible and has been used at various sites: The Savannah River Site (F and H areas) and Los Alamos National Laboratory in the United States, and the Mayak RT-I plant in Russia have used Pu(III) oxalate precipitation. Process conditions for the Pu(IV) oxidation state precipitation must be more closely controlled but the decontamination across the Pu(IV) precipitation is better than with Pu(III) precipitation; the solubility of the hydrated Pu(III) oxalate product is less; therefore plutonium losses are less (see Table XXX).

Hydrogen peroxide can also be used to precipitate the Pu(IV) and HF can be used to precipitate Pu(III).

Decontamination factors for plutonium by precipitation method are given in Table XXX. [Katz 1986, Cleveland 1979, Gray 2012]

Table XXX Decontamination factors for plutonium by precipitation method

Element	Pu(III) Oxalate	Pu(IV) Oxalate	Pu(IV) Peroxide	Pu(III) Fluoride
Fe	33	10	50	1.4
Co	47	>95	30	8.6
Zr	3.5	>44	1	1.1
Mo	>13	>15	>140	1.1

Ru	>38	33	>14	36
Ce	1	1	6	1.1
Th		1		
Al		100		
Ni		100	>3,000	
Cr		100	>7,000	
U		60		

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II.E.1 Oxalate Precipitation Processes

Both Pu(III) and Pu(IV) can be precipitated by the addition of oxalic acid. The Pu(IV) oxalic acid procedure is the more difficult to control but gives better decontamination. Both procedures have been effectively used on an industrial scale and are discussed below.

II.E.1.1 Pu(III) Oxalate Precipitation

The Los Alamos National Laboratory, and the Savannah River Site in the United States and the Mayak plant in Russia precipitated Pu(III) oxalate as the route to plutonium oxide. Precipitation can be accomplished from solutions containing as little as 1 g Pu/L and not more than 4M HNO₃. If the feed contains Pu(IV) it must first be reduced to Pu(III); this reduction can be accomplished using hydroiodic acid, hydroxylamine, hydrazine or other reducing agents. [Wick 1967, Cleveland 1980, Gray 2012, Cleveland 1970, Cleveland 1979, Gray 1999, Burney 1984, Bradley 1997, Porter 1965, Smith 1976, Rankin 1975, Burney 1982, Abrahamson 1967, Doty 1970, Barr 1970, Cadwell 1968, Louwier 1976, Long 1978] Precipitation conditions are not critical; the oxalic acid can be added as a solid or in solution and as rapidly as desired. Also, the oxalic acid can be added to the plutonium solution (direct strike) or the plutonium can be added to the oxalic acid solution (reverse strike). The Savannah River Site added solution to a two-stage precipitator. After an approximately half-hour digestion period, the precipitate is filtered, washed with water, and dried. Filtrate losses are low.

At the Mayak plant (Figure XXX), the final PUREX plutonium solution is about 20 to 30 g of Pu/L, hydrazine is added to assure that plutonium is in the Pu(III) oxidation state and is batch precipitated using oxalic acid as the precipitant. This product is dried and calcined to PuO₂. [Bradley 1997]

Work on the production of ²³⁸PuO₂ fuel forms^{††††††††} has shown that widely different particle morphologies and sizes can be obtained from oxalate precipitation depending on a variety of factors. [Burney 1984, Porter 1965, Smith 1976, Bickford 1976, Smith 1976, Rankin 1975, Burney 1975, Abrahamson 1967, Doty 1970, Barr 1970, Caldwell 1968, Louwrier 1976]. These include

A. Valence of the plutonium in solution

^{††††††††} Burney [Burney 1984] found no differences between ²³⁹Pu and ²³⁸Pu.

- B. Mixing sequence of plutonium nitrate and oxalic acid
 - a. Direct strike: adding oxalic acid solution into Pu(III) nitrate solution yields rosette aggregates
 - b. Reverse strike: adding Pu(III) nitrate solution into oxalic acid solution yields monoclinic laths
- C. Variables affecting initial supersaturation (nucleation rate) and the final solubility (particle growth rate)
 - a. Precipitation temperature
 - b. Plutonium concentration in the feed
 - c. Oxalic acid concentration in the feed
 - d. Final oxalic acid concentration in slurry
 - e. Agitation vs. no agitation

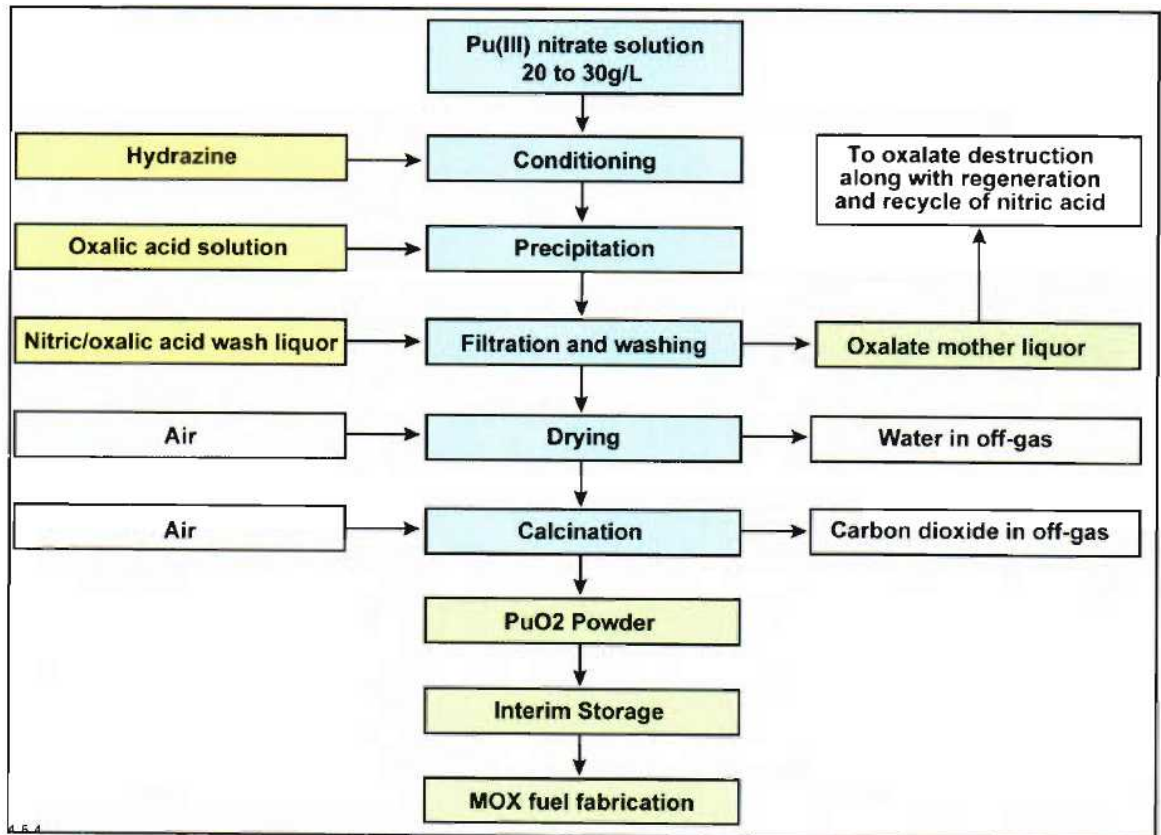


Figure 28.XXX Mayak flow sheet for Pu(III) oxalate precipitation [Bradley 197]

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II.E.1.2 Pu(IV) Oxalate Precipitation

The compound $\text{Pu}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$ may be precipitated satisfactorily over a relatively wide range of acidities, from HNO_3 solutions containing from 1 to 300 grams Pu per liter. [Wick 1967, Cleveland 1980, Gray 2012, Cleveland 1970, Cleveland 1979, Gray 1999, Long 1978] In a commercial plant the final desired product is PuO_2 . A typical commercial flow sheet of Pu(IV)-oxalate precipitation appears in Figure XXX.

The feed solution must contain sufficient nitric acid (HNO_3) to make the final

slurry acidity 1.5 to 4.5M. [Cleveland 1980] Lower acidities favor co-precipitation of impurities, and also result in a precipitate that is too finely divided for rapid settling and filtration. Higher acidities result in a thixotropic (gummy) precipitate and high filtration losses due to the increased solubility of the precipitate.

The plutonium solution is heated to about 50°C and treated with H₂O₂ to adjust all plutonium to the tetravalent state, the rate of addition being limited by the extent of foaming due to peroxide decomposition. Although the rate of this reaction can be very slow at room temperature, especially for dilute plutonium solutions, it is rapid at 50°C.

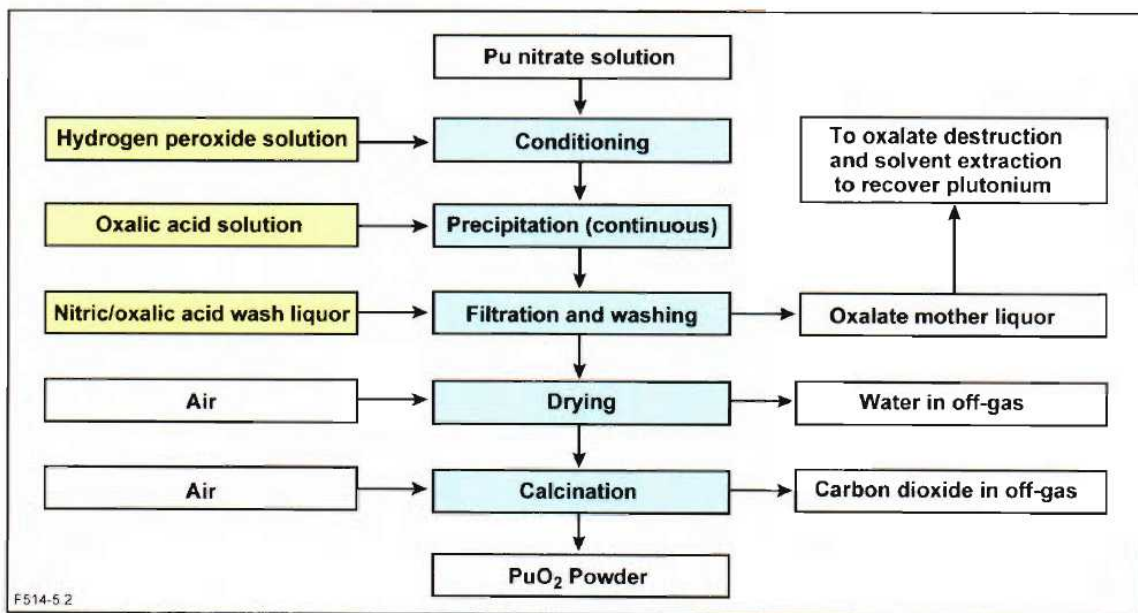


Figure XXX Flowsheet for Pu(IV) oxalate precipitation

Precipitation is accomplished by the addition of a 1 M oxalic acid solution, over a period of 10 to 60 minutes, until the final slurry has a free oxalic acid concentration of 0.05 to 0.15M. Also critical is the temperature of precipitation, which must be in the 50 to 60° C range. Too low a temperature or too rapid an addition of precipitant may produce a precipitate that is too finely divided for rapid filtration, while temperatures above 60° C often result in thixotropic precipitates. Because of the rapidity of the valence adjustment reactions at these temperatures, the H₂O₂ and oxalic acid solutions may be combined and added together.

After completing the addition, the crystals are allowed to "digest" or "age" for 10 to 60 minutes at the same temperature to allow the crystals to grow. The precipitate is then filtered and washed with dilute solution of nitric and oxalic acids. The resulting cake contains approximately 99% of the plutonium originally present in the feed.

The mother liquor passing through the filter contains the residual plutonium. This solution is concentrated by evaporation and then refluxed with concentrated nitric acid to oxidize the residual oxalic acid to CO₂ before the plutonium residue stream is fed back into the PUREX process for recovery and purification.

At the Hanford Site the precipitate was collected on a rotating filter, which is continuously scraped; the precipitate drops from the filter into a drying furnace where it is moved along by an internal Archimedes screw. Excess water was first removed, followed by the waters of crystallization, followed by thermal decomposition of the oxalate to give PuO₂. This rough product then passed into a second "calcination" furnace, where the temperature is controlled at approximately 600° C reduced the surface area of the PuO₂ powder to around 10 m² per gram. The desired surface area was somewhat a balancing act: a high specific surface area improves the homogeneity of the MOX fuel when fabricated; too high a surface area increases the capacity for adsorption of moisture.

II.E.2 Plutonium Peroxide Precipitation

Early development work at the Los Alamos National Laboratory indicated that plutonium could be efficiently concentrated and purified by peroxide precipitation. The method was fully developed for use the Los Alamos National Laboratory [Leary 1959, Morgan 1958, Widner 2009], the Rocky Flats Plant [Thompson 1972, Miner 1972, Hagan 1972, Hagan 1974, Hagan 1975, Greinetz 1980], and the Savannah River Site [Moore 2000]. A version of a flowsheet from the Los Alamos National Laboratory is given in Figure XXX [Leary 1959]

Plutonium peroxide is a nonstoichiometric compound whose composition and crystalline modification are dependent on precipitation conditions. [Wick 1967, Cleveland 1980, Cleveland 1970, Cleveland 1979, Leary 1959, Connick 1949] The precipitant solution is typically 30 to 50% H₂O₂ and the plutonium solution typically is < 5M HNO₃ (can vary from 2.5 to ~5.0 M) and 0.05 to 1M SO₄²⁻.

- At higher nitric and sulfuric acid concentrations and with careful H_2O_2 addition, a very filterable hexagonal form of plutonium peroxide precipitates. Plutonium peroxide is soluble at acidities greater than $\sim 5\text{M}$. [Hopkins 1949, Koshland 1949]
- At lower acidities a gelatinous cubic form precipitates that is difficult to filter.

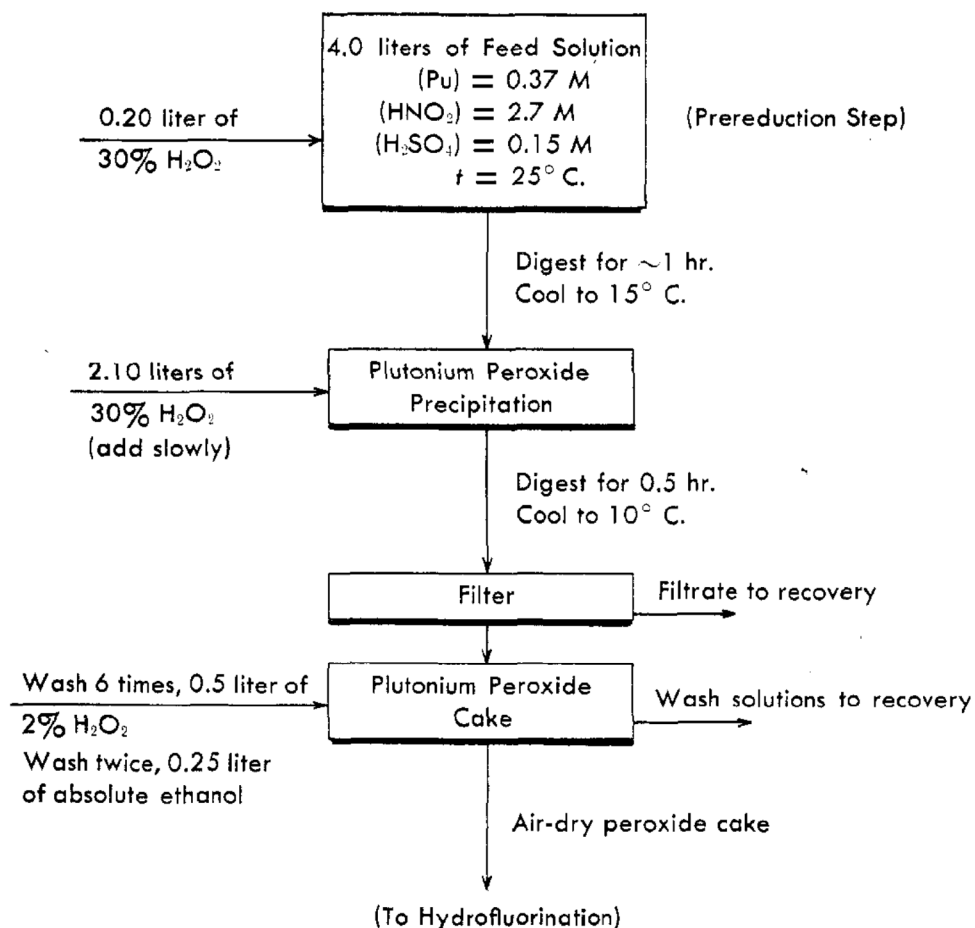


Figure 1. Precipitations were carried out in a remotely controlled plant

The temperature was typically controlled between 10 and 15°C. Typically sufficient H_2O_2 was added to convert all plutonium ions to Pu(IV) ; the reaction is slow and typically requires about one hour. Further addition of H_2O_2 produces first a brown complex ion, $[\text{Pu}_2(\text{O}_2)(\text{OH})]^{5+}$. Continued addition of H_2O_2 results in the formation of a red complex ion, $[\text{HO-Pu-OO-Pu-OOH}]^{4+}$. Continued

addition of H_2O_2 results in the precipitation of green plutonium peroxide. [Leary1959] Plutonium peroxide is not a stoichiometric compound and its O:Pu ratio may approach 3.5 [Cleveland, 1979; Cleveland, 1980], but does not reach 4.0 as is suggested by the formula $\text{Pu}(\text{O}_2)_2$. Anions such as nitrate, chloride and sulfate, if present in the solution, are incorporated into the solid. Indeed, sulfate is added in some process solutions to improve the filterability of the peroxide precipitate.

- The precipitate was typically digested for about half an hour at reduced temperature and then filtered.
- The excess H_2O_2 in the filtrate was typically decomposed by heat.
- The precipitate was normally washed several times with dilute H_2O_2 and sometimes with absolute ethanol.
- Pulling air through it then typically dries the washed precipitate.

Note that under certain conditions, which are not understood, the solid can breakdown into a liquid with a syrupy consistency. Since this behavior is unpredictable, the possibility of its occurrence must be considered in planning equipment to be used in handling the material.

The major advantages of peroxide precipitation over other precipitants are:

- The higher decontamination factor attained from many impurity elements except thorium, neptunium, and uranium that form similar peroxide precipitates under these conditions. Americium, in particular, is removed because it does not form a solid peroxide compound. [Leary 1959]
- H_2O_2 does not add other impurities to the stream
- H_2O_2 is readily destroyed by boiling
- Optimal particle size formation for successive fluorination.

Typical decontamination is given in Table XXXX.

Table XXX. Typical Decontamination of Plutonium via Peroxide Precipitation [Thompson 1972]

Element	Parts of Element per 10^6 Parts Plutonium		Decontamination Factor (DF)
	Nitrate Feed	Pu Peroxide	
Al	2088	21	99
Be	1.7	<0.05	>34
Cr	1116	16	70
Cu	681	4	170
Fe	7804	141	55

Ga	2092	24	87
Ni	1418	27	52
Pb	525	<2	>262
Si	722	19	38

The disadvantages to peroxide precipitation are:

- Filtrate losses can be higher than other processes (typically 0.1 to 0.5%)
- H₂O₂ can decompose violently in the presence of certain metal impurities (Fe, Cu, Mn, Ni, etc.) requiring refrigeration during precipitation and control of the impurities
- The precipitate is not stable and decomposes
- A high calcination temperature (950° C) is required to volatilize sulfate, if present
- Halogens, nitrates and especially sulfates are carried in the crystal lattice, depending on the precipitation medium [Leary 1959, Hamaker 1949]

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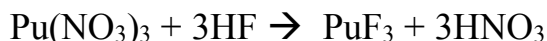
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II.E.3 Plutonium(III) Fluoride Precipitation

The PuF_3 may be precipitated as a crystalline material, easy to filter and dehydrate, but only by careful control of chemistry and equipment engineering. [Wick 1967, Cleveland 1980, Gray 2012, Cleveland 1970, Cleveland 1979, Gray 1999, Long 1978] The trifluoride precipitation optimizes these conditions to produce a product that is readily amenable to plant-scale processing. However, the trifluoride precipitation is less capable of decontamination of impurities than other precipitation methods and results in higher operator exposure.

The equation for trifluoride precipitation may be written as:



Since a Pu(III) solution is required, the process is most suitable for cation-exchange eluate, but any plutonium solution may be used if the plutonium is first reduced to the trivalent state. As the solubility of the tetrafluoride is over 600 mg/L, compared to about 10 mg/L for the trifluoride, it is important that the Pu(IV) content be kept low to minimize filtrate losses. To ensure that Pu(IV)***** was not present, the Savannah River Site treated the plutonium solution from the solvent extraction/cation exchange processes with sulfamic acid and ascorbic acid to reduce any residual Pu(IV) to Pu(III). In addition, high Pu(IV) content can result in increased filtration time. Even in HNO₃ solutions containing sulfamic acid, Pu(III) oxidizes to Pu(IV) at a rate of about 6% per day (until about 42% is in the tetravalent state), thus making it necessary to reduce aged solutions before precipitation. The addition of 0.05 M of ascorbic acid per liter of plutonium solution, about 30 minutes before precipitation, will reduce all the Pu(IV) to the trivalent [Pu(III)] state and hold it in this oxidation state.

Since HF is a weak acid, the solubility of Pu(III) is a function of the HNO₃ /HF ratio. Therefore, precipitation conditions may be expressed conveniently in terms of HNO₃ /HF ratios. Conditions of moderate solubility or high HNO₃/HF ratios favor crystal growth, while a low HNO₃/HF ratio is necessary to minimize filtrate losses. These contradictory requirements are met by conducting the precipitation in two stages.

The feed solution, 4 to 5 M in HNO₃ and containing 30 to 70 g of Pu(III) per liter, and HF are added simultaneously, at carefully controlled rates, to the first-stage precipitation vessel. Although 2.7 or 4 M HF is normally used, the concentration is not critical, provided the rate of addition is controlled. The rate of agitation in the precipitator is important; it must be sufficiently rapid to minimize local concentration irregularities, but must not be so great as to result in a precipitate that is too finely divided. The optimum agitator speed depends on the precipitation vessel design, but in general will be in the range of blade-tip

***** Precipitation of Pu(IV) from aqueous solution gives the hydrate, PuF₄ · 2.5H₂O, which also affects downstream operations. For instance, the hydrate tends to form "rocks," which are sufficiently large to plug process lines. The hydrate does not dry well.

speeds of 2 to 5 ft/sec. At the Savannah River Site, for good performance, this corresponded to roughly equivalent to agitator speeds of about 280 rpm in the first stage and about 400 rpm in the second stage precipitator.

Solution additions in the first-stage precipitator were controlled so as to achieve a HNO_3/HF ratio of six or higher. Excessive HF, or lower ratios, can cause rapid nucleation and result in excessive "fines" generation, which can plug filters and increase filtration times, while the upper limit depends on the degree of agitation. If the HNO_3/HF ratio is too high, the crystals formed are so large as to be difficult to suspend and transfer. Deficient HF can cause the interior surfaces of the precipitator vessels to become sites for crystal growth, i.e., "plating." Plated material builds up on those surfaces and eventually flakes off resulting in plugged process lines.

The rate of addition of feed and HF must be controlled to allow for adequate residence time in the first stage precipitator for adequate crystal growth to take place. For a 50-60-g/L feed, the first-stage residence time must be at least 5 minutes. The slurry then overflows into the second-stage precipitator, where sufficient HF is added to lower the HNO_3/HF ratio to three or less and complete the precipitation.

In both of the first- and second-stage precipitation vessels, it is important that the precipitate not be permitted to settle to thicknesses greater than about 1 cm. Thicker deposits will prevent penetration of the holding reductant and thus allow the precipitate to be oxidized to the tetrafluoride by HNO_3 .

The slurry is removed from the second-stage precipitator and filtered, immediately after which it is thoroughly washed with dilute (0.8M) HF to remove all HNO_3 , which can slowly oxidize the plutonium trifluoride. Typically, the damp cake is dried in a stream of air at 70-100°C for 3-4 hours to reduce the moisture content to below about 2%.

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II.E.4 Direct Denitration

In Japan, plutonium is co-converted with uranium in a microwave-assisted thermal denitration process in the current small-scale finishing and fabrication plant at Tokai-Mura and the commercial-scale reprocessing plant at Rokkasho-Mura (Figure xxx).

- The uranyl nitrate solution is concentrated by evaporation and then fed to a fluidized-bed reaction tower to decompose the uranyl nitrate to UO_3 powder. The uranyl nitrate solution is sprayed into the fluidized bed and electric heaters thermally decompose the solution at approximately 300°C .
- The plutonium nitrate solution is blended with uranyl nitrate solution equal to the plutonium content that is then concentrated and denitrated using microwave heating. The mixed uranium-plutonium denitrated powder is then heated to approximately 800°C , first in an air atmosphere in the electrically heated calcination furnace, and then to

For microwave heating, the same frequency is used as in a home microwave oven.

approximately 800°C in mixed nitrogen-hydrogen atmosphere in an electrically heated reduction furnace to produce MOX powder. This resulting uranium and plutonium oxide is blended, loaded into powder cans, and stored.

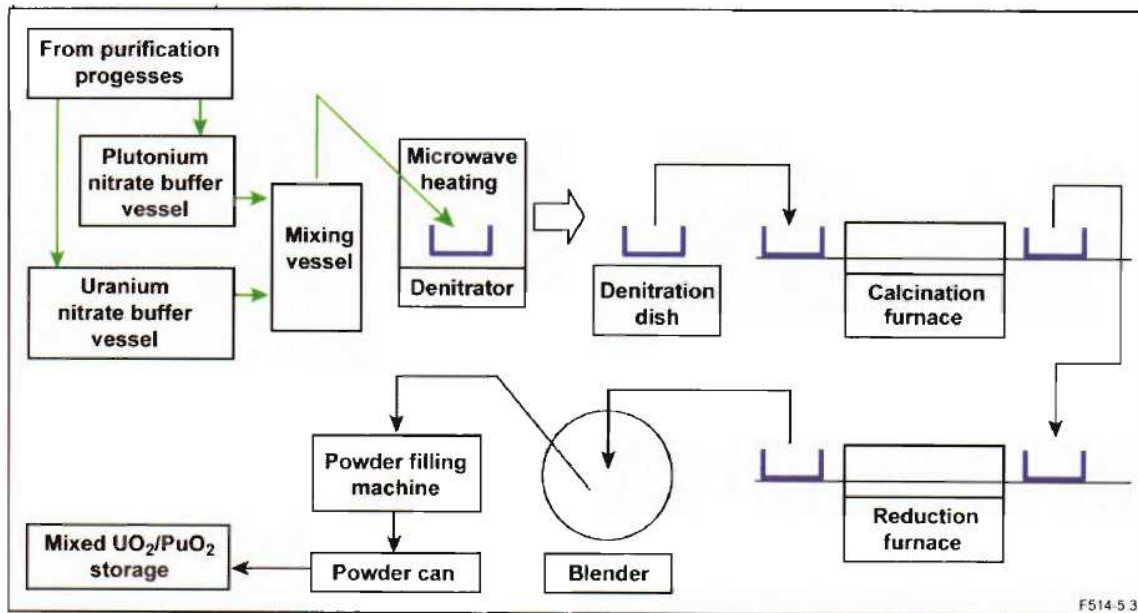


Figure XXX Japanese flowsheet for plutonium-uranium denitration from purification processes

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II.F Conversion To Products

There are only two stable end products that have been used at the industrial scale:

1. Plutonium dioxide, PuO_2 . This compound is normally referred to as simply plutonium oxide. Plutonium oxide can be used as a long-term stable storage product or as feedstock for the fabrication of MOX fuels.
2. Plutonium metal, which is the preferred form for fabrication of weapons, was also used in many physics experiments.

II.F.1 Conversion to Oxide

Plutonium oxide is typically produced by calcining either Pu(III) oxalate or Pu(IV) oxalate. For short term storage, subsequent conversion to metal, or to MOX fuel the oxalate is calcined at less than 550 to 600°C for subsequent conversion to metal or to MOX fuel. For long-term storage, the plutonium oxalate is typically calcined in excess of 900°C.

II.F.2 Conversion to Metal

For weapons production and some physics experiments, the isolated plutonium must be converted to metal. [Wick 1967, Cleveland 1980, Gray 2012, Cleveland 1970, Cleveland 1979, Gray 1999, Katz 1986, Harmon 1961, Leary 1966, McCreary 955, Long 1978] Plutonium metal may be produced by thermite-type reaction of a reactive metal (may be an alkali or alkaline earth metal but typically calcium or magnesium) with a plutonium fluoride salt at elevated temperature in a sealed metal pressure vessel (called a "bomb"). The metal

product is freed from the slag, pickled or washed in concentrated HNO_3 to remove residue, washed with water, dried, and then re-melted in a high-temperature furnace and cast into shapes from which weapon components are fabricated.

Preparation of plutonium metal by reduction of a plutonium fluoride with an alkaline earth metal in a sealed pressure vessel is the only facet of plutonium chemical processing that has remained unchanged over the years. The sealed pressure vessel (bomb), capable of withstanding pressures of 50 – 400 psig and temperatures of up to $1,600^\circ\text{C}$, is purged thoroughly with an inert gas (usually argon) and sealed. Furthermore, air has to be excluded from the bomb, as its presence results in a poorly formed button of low yield.

II.F.2.1 Conversion to Metal from Fluoride Salts

Plutonium metal may be obtained by numerous reactions. Reviews by Katz [Katz 1986], Cleveland [Cleveland 1979], Harmon, et al. [Harmon 1961], Leary, et al. [Leary 1966], and McCreary, et al. [McCreary 1955] give summaries of such reactions. Not all reactions discussed in the referenced articles are useful in production work. Useful reactions:

- Produce a dense, coherent mass of pure plutonium in high yield
- Evolve sufficient heat to melt both the metal and the resulting slag
- Result in a slag that stays molten and non-viscous long enough to allow the plutonium to coalesce
- Work on a scale desired (a reaction suitable for microgram-scale reductions might be less useful for gram- and multi-gram-scale reductions, and vice-versa)

The reduction of plutonium fluorides with calcium has proven to be the best method to use for production of plutonium metal. The Hanford Site, Rocky Flats Plant, and the Los Alamos National Laboratory in the United States preferred to use PuF_4 as the starting material. The Savannah River Site [Gray 1986] used a mixture of PuF_4 and PuO_2 for their starting material. Even if a site uses the predominately PuF_4 route to plutonium metal, there are varying amounts of PuO_2 present. The United Kingdom and France have used PuF_4 as the starting material for metal production.

Two routes to produce PuF_4 have been used:

- Via plutonium(IV) oxalate precipitation, and
- Via plutonium peroxide precipitation.

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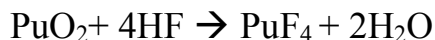
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II.F.2.2 Fluorination. At Hanford, the PuO₂ powder dropped from the screw

calciner into a vibrating tube fluorinator. Metered streams of hydrogen fluoride (HF) gas and oxygen (O₂) gas were introduced into the fluorinator tube. The HF reacted with the PuO₂ according to the following reaction:



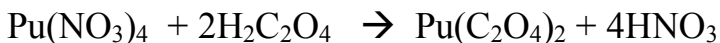
Small quantities of hydrogen (H₂) gas present as an impurity in the HF gas, tends to favor the formation of PuF₃. Hence, O₂ gas was introduced along with the HF to prevent the formation of a reducing atmosphere. Heaters were used to maintain a temperature of the reactants at about 525°C. The PuF₄ powder was collected for downstream processing.

At the Rocky Flats Plant the PuO₂ was converted to PuF₄ in a similar manner as described above for Hanford. The conversion was conducted in a rotary-tube fluorinator with HF gas added to the fluorinator to react with the PuO₂ at 300° – 650°C. [Standofer et al. 1972].

II.F.2 .2.1 Conversion to Metal From Plutonium (IV) Oxalate

The Hanford Site provides an example of plutonium(IV) oxalate as the feed source in the conversion of plutonium(IV) to plutonium metal. The Hanford Plutonium Finishing Plant (PFP) received feeds from three different sources: the PUREX and REDOX processes in which the product was evaporated to approximately 350 - 400 g of Pu/L and transported to the PFP and from the Plutonium Recovery Facility (PRF) where plutonium was recovered in a PUREX-type system in which the diluent was carbon tetrachloride instead of n-paraffin. [Wick 1967, Cleveland 1980, Gray 2012, Cleveland 1970, Cleveland 1979, Gray 1999, Long 1978, Lini and Rogers 2002]

The main process control variables in this conversion system were the nitric acid and oxalic acid molarities of the final slurry overflowing the precipitation reactor. To obtain readily filterable slurries with low plutonium losses to the filtrate, a nitric acid molarity of ~3.0 M and an oxalic acid molarity of ~0.1 M are desirable. The quantity of oxalic acid stoichiometrically required is calculated from the equation:

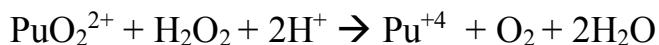


Hence, the oxalic acid flow rate required is dependent on the flow rate of the

feed solution and its plutonium concentration; and the feed nitric acid concentration is dependent on the plutonium concentration.

The feed nitric acid concentration is adjusted upwards, if required, by adding a calculated quantity of 12M HNO₃ or downward with a calculated quantity of 0.5M HNO₃. Distilled water is not used directly because of the possibility of forming plutonium polymer in the plutonium solution.

In addition to the acidity adjustment, each batch must be treated with 12% to 15% hydrogen peroxide to reduce any plutonium present in the Pu(VI) valence state to the Pu(IV) valence state. In strong acidic solutions the amount of Pu(VI) is typically small, but would still result in high losses of plutonium to the filtrate. This reaction takes place as follows:



Some impurities, especially iron, present in the feed will catalyze the decomposition of H₂O₂. Hence, the H₂O₂ addition must be controlled and the addition performed with agitation to minimize foaming. The dilution resulting from the H₂O₂ addition must be taken into account in the acidity adjustment calculation. The plutonium nitrate solution and the oxalic acid solution are pumped continuously and simultaneously into the precipitator, where they are mixed and the plutonium oxalate hexahydrate precipitate formed. The precipitate is filtered and washed with a solution of 2M nitric acid and 0.05M oxalic acid.

At Hanford, the precipitate was dried and calcined at a temperature of 350° to 400°C in a screw calciner. The overall calcination reaction is as follows:



II.F.2 .2.2 Conversion to Metal From Plutonium (IV) Peroxide

Plutonium peroxide was investigated by Hamaker and Koch [Hamaker and Koch 1949], Hopkins [Hopkins 1949], and Koshland et al. [Koshland et al. 1949] in the 1940's and Leary [Leary 1954] in the early 1950's. The Rocky Flats Plant precipitated plutonium (IV) peroxide [Baldwin and Navratil 1982] from solution using H₂O₂. The Rocky Flats Plant feed was a mixture of anion-exchange eluate and nitrate solution from dissolution of impure PuO₂. [Martella et al 1984] The peroxide precipitation also was used at Los Alamos National Laboratory and the Savannah River Site. The main process advantages for the Pu(IV) peroxide precipitation at the Rocky Flats Plant [Martella et al 1984, Hagan and Miner

1980]

- No additional impurities were introduced by the use of H₂O₂ as the precipitant
- The peroxide precipitation reaction was quite specific for plutonium
 - decontamination of americium below appreciable limits in the plutonium precipitate
 - highest decontamination from most cationic impurities of all precipitation methods
- H₂O₂ was readily destroyed by boiling
- Particle size was optimal for subsequent fluorination

The major chemical disadvantages to the process included: [Martella et al 1984]

- Violent decomposition of H₂O₂ if certain impurities were present (e.g., iron, copper, and manganese)
- Decomposition of the precipitate
- Filtrate losses were high
- Halogens and nitrates were carried into the crystal lattice.

The major operational disadvantages included: [Martella et al 1984]

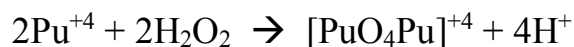
- Rigid control of the H₂O₂ addition was essential
- Refrigeration of the feed was required to prevent peroxide decomposition
- Decomposition of the plutonium peroxide could adversely affect filtration
- Handling solid and dissolved peroxides could be unstable under certain operating conditions.

In general, the peroxide precipitation can be considered to proceed in three phases.

1. In the initial phase, small amounts of H₂O₂ are added to the plutonium nitrate solution causing a brown complex to form as noted below [Leary 1954].



2. As more H₂O₂ is added, the brown complex changes to a red complex that contained two peroxy-oxygen atoms per plutonium atom. [Hagan et al 1975]



3. With further addition of H_2O_2 , the red complex disappears and the green plutonium peroxide precipitate forms. [Hagan et al 1975]



At the Rocky Flats Plant, the plutonium nitrate feed solution (~20 to 100 grams/liter Pu) was adjusted to ~ 4.0M in HNO_3 and 0.04M with respect to sulfate ion concentration.[Martella et al 1984] The adjustment to ~4.0 M nitric acid favors the formation of a hexagonal-phase precipitate which is more dense and easily filtered than precipitate phases formed under lower acid conditions (<2M nitric acid) at which a colloidal face-centered cubic phase precipitate forms) and at higher acid conditions (>5M nitric acid) at which the plutonium peroxide is soluble. [Martella et al 1984].

The formation of a more filterable precipitate is favored by the slow and uniform addition of the H_2O_2 and slow mixing. At the Rocky Flats Plant, the initial H_2O_2 was added at a rate of 3 liters/hour along with slow mixing to achieve the more filterable precipitate. In addition, a several-fold excess of H_2O_2 to plutonium rate is needed to assure complete precipitation of the plutonium. At the Rocky Flats Plant, an excess of at least 10 moles H_2O_2 per mole plutonium was added using a 35% solution of H_2O_2 at 10 liters/hour [Martella et al 1984].

At the Rocky Flats Plant, during the precipitation process, the temperature of the solution was kept at less than 15°C to prevent any metallic impurities from catalyzing the decomposition of the H_2O_2 . [Martella et al 1984].

At the Rocky Flats Plant plutonium peroxide precipitation was a continuous process in which the H_2O_2 solution was slowly added to the plutonium nitrate solution in a cooled reaction vessel. The resulting slurry overflowed into another cooled vessel. Both vessels were stirred to assure adequate mixing. The slurry from the second vessel overflowed onto a continuous rotary vacuum drum filter. The precipitate collected on a polypropylene filter cloth. The precipitate was washed continuously with a 0.35M HNO_3 solution. A scraper blade removed the precipitate from the filter cloth. The precipitate was transferred to a furnace and calcined at 450°C for two hours to convert it to plutonium oxide. The furnace was an electrically heated rotary tube furnace. The plutonium peroxide was fed to the furnace feed hopper, which used a screw feeder to convey the plutonium peroxide into the furnace tube.

Boiling the filtrate destroyed any remaining peroxide.

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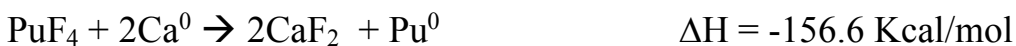
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II.F.2.3 Bomb Reduction of PuF₄. At the Hanford Site the PuF₄ powder was blended with calcium metal plus a small amount of iodine and then reduced to metallic plutonium in a hermetically sealed pressure vessel. The reactions that took place during the reduction are as follows:



The iodine booster was added to provide the dual benefit of increasing the heat of reaction and lowering the melting point of the slag, thereby aiding metal coalescence. MgO sand was used to pack the loaded crucible into the furnace. The crucible was MgO ceramic.

The reduction charge consisted of:

- PuF₄
- A small amount of PuO₂ impurity
- A stoichiometric quantity of finely divided calcium metal plus an excess
- A small quantity of iodine, which depends on the scale of reduction.

It is very important that the PuF₄ be dry and anhydrous to prevent dangerously high pressures in the pressure vessel during the reduction, and to prevent a reduction in yield from the formation of PuO₂.

When prepared, the pressure vessel was purged thoroughly with argon and sealed. Air had to be excluded from the pressure vessel as its presence resulted in a poorly formed plutonium button and a low yield. Also, plutonium buttons prepared in the presence of air or moisture tends to be pyrophoric.

The bomb was heated slowly; the charge fires when the temperature of the chemicals reach approximately 550°C. On firing, the internal temperature rapidly climbed to about 1,500°C and there was an immediate reduction in the neutron field resulting from the dissociation of the fluoride ions from direct bonding with plutonium. The PuF₄ powder was reduced to molten metal, which

coalesced into the crucible bottom. The slag solidified at about 1,400°C (see Figure 6-31).

As with Hanford, the Rocky Flats Plant produced plutonium metal from PuF₄ using a thermite reaction in a hermetically sealed pressure vessel. Calcium was used as the reducing agent. MgO sand was used to pack the loaded crucible into the furnace. The crucible was MgO ceramic. Instead of iodine as an initiator, RFP used a mixture of powdered magnesium, sodium peroxide, and potassium iodate, referred to as a pyrotechnic initiator. [Wastren 1998]

After loading, the pressure vessel was evacuated and back-filled with argon. The pressure vessel and its contents (the bomb) [Long et al 1972] was heated slowly to 300° – 400°C; the pyrotechnic initiator assisted with the reaction onset and upon firing, the internal temperature rapidly climbed to about 1,500°C and there was, just as with Hanford, an immediate reduction in the neutron field. The plutonium in the PuF₄ powder was reduced to a molten metal, which coalesced into the crucible bottom. The slag solidified at about 1,400°C.

II.F.2.3 Button Finishing. At Hanford, the pressure vessel was cooled, opened, the crucible removed and broken open, and the metal button, sand, slag, and crucible fragments (SS&C) separated. The SS&C was assayed to determine the plutonium content and if the plutonium content was sufficiently attractive, the SS&C would be dissolved to recover the plutonium. The metal button was pickled in nitric acid and rinsed in water. The nitric acid pickling step dissolved the slag via the reactions:



After water rinsing, the button was dried before it was sampled and packaged.

At the Rocky Flats Plant, the plutonium metal button was recovered and treated as described for Hanford.

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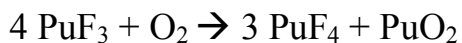
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II.F.2 .4 Conversion to Metal from Plutonium Trifluoride

Dry PuF₃ may also be roasted in oxygen to yield a mixture of PuF₄ and PuO₂, [Wick 1967, Cleveland 1980, Gray 2012, Cleveland 1970, Cleveland 1979, Gray 1999] according to the equation



The Savannah River Site used PuF₃ as the plutonium source for the conversion to metal because of the following advantages:

- Filtrate plutonium content was normally so low (0.05 to 0.1 %) that the filtrates may be discarded without recovery.
- The process involved solids and solutions that were more stable with

- respect to spontaneous decomposition than those encountered in the peroxide process.
- The process avoided the corrosion problems associated with the use of iodine.
 - The oxygen roasting process had the advantage of requiring and producing no corrosive materials.
 - The lower reduction yield (93% for PuF_4 / PuO_2 versus ~97% for PuF_4) was not necessarily a commanding disadvantage; plutonium must be recovered from the SS&C residue regardless of which reduction procedure was used, and the extra plutonium present in the SS&C did not pose a handicap.

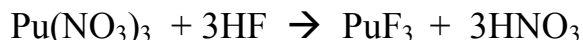
There were also some disadvantages to the PuF_3 precipitation route to metal:

- It required the use of concentrated HF solution, a corrosive reagent. As a result, all equipment had to be constructed of special corrosive-resistant materials.
- The equipment became caked with deposits of plutonium fluorides, which had to be removed frequently by washing with an $\text{Al}(\text{NO}_3)_3\text{-HNO}_3$ solution. Appreciable volumes of this wash solution were used, and all of it had to be processed to recover the plutonium. Moreover, the aluminum in the wash solution subsequently had to be removed completely from the equipment before future runs to avoid contaminating the plutonium product.
- The PuF_3 precipitation process did not attain the degree of decontamination from cationic impurities as the peroxide and oxalate processes.

The Savannah River Site FB-Line received purified plutonium nitrate solution from the PUREX second plutonium solvent extraction cycle. The plutonium valence in the solution was Pu(III) and that valence was maintained by having a dilute presence of hydroxylamine nitrate. The plutonium concentration in that solution was about 1.5 to 2.0 grams/liter. Cation ion exchange was used to concentrate the Pu(III). The cation ion exchange eluate had a Pu(III) concentration of 25 to 30 grams/liter. (Molen and Gray 1986)

The PuF_3 was precipitated by the simultaneous addition of a 10.4M hydrofluoric acid solution and the concentrated plutonium (III) nitrate solution to a precipitator tank. The addition was controlled to minimize the number of PuF_3 nuclei formed and the solutions overflowed to a second precipitator tank to which was added a 1.7% HF solution. The precipitation was according to the

equation:



That addition was controlled to favor the precipitation of large PuF_3 crystals. Vessel After filtration, the precipitate was washed.

The air-dried cake is roasted first in an inert atmosphere at 150-200°C and then in an oxygen atmosphere at 400°C. The resulting mixture of PuF_4 and PuO_2 [which contains a greater fraction of PuO_2 than indicated by the above equation] may be reduced without the use of iodine booster although at somewhat decreased yield. The yield at Savannah River was approximately 93%.

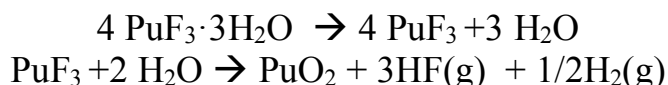
II.F.2.3.1 Drying and Conversion. At the Savannah River Site the PuF_3 cake was then transferred in its filter boat to an air-drying station. At this point, the filter cake contained from 15 to 40% moisture depending on the conditions of the precipitation. If the conditions were good, the moisture content was less than 25%. Warm, dry air was drawn through the cake to remove residual moisture. Air-drying of the cake ensured conversion without excessive hydrolysis during the subsequent roasting step. After air-drying, the moisture content varied from 2 to 6%. Good reduction yields were dependent on good drying of the filter cake. Poor drying could lead to clumping of the cake. These clumps lead to low yields due to:

- Hydrolysis of the cake in the conversion step
- Hydrolysis of the calcium added for the reduction step
- Incomplete reduction due to poor reduction kinetics

The resulting air-dried cake had a composition of $4\text{PuF}_3 \cdot 3\text{H}_2\text{O}$ (i.e., 4.4% water). This material is hygroscopic enough to gain water (if exposed to a humid atmosphere) to approximately the composition $5\text{PuF}_3 \cdot 6\text{H}_2\text{O}$ (6.4% water).

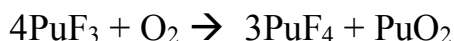
Air-dried cakes were combined and transferred to the roasting furnace. As too rapid or excessive drying in the presence of oxygen could lead to hydrolysis, residual water and other volatile materials were initially removed at a low initial temperature ($\sim 150^\circ\text{C}$) and were swept from the furnace with a nitrogen stream.

The potential hydrolysis reactions were:



The rate of hydrolysis is proportional to the partial pressure of water in the air-drying furnace atmosphere. Roasting in a dynamic nitrogen atmosphere at 150-200°C removed additional water while minimizing hydrolysis.

After the initially heating in the nitrogen atmosphere at 150-200°C, the material was then roasted in an oxygen atmosphere at 400°C with the following reaction:



The theoretical ratio is 75 mole% PuF₄ and 25% PuO₂. At the Savannah River Site, the actual ratio obtained was typically 73 mole% PuF₄ and 27% PuO₂. The entire processing line at this point had to be kept dry.

II.F.2.3.2 Bomb Reduction of PuF₄/PuO₂ Mixtures

As with the Hanford Site and the Rocky Flats Plant, the Savannah River Site used a bomb reduction process to produce plutonium metal. However, the Savannah River Site used a mixture of PuO₂ and PuF₄. The plutonium feed was mixed with an excess of finely divided calcium metal, placed into a MgO ceramic crucible, and the loaded crucible placed into a pressure vessel (bomb). The furnace charge was evacuated and backfilled with argon. The amount of excess calcium depended on the scale of the reduction reaction. At the Savannah River Site, the reduction was performed without the use of the iodine booster resulting in a somewhat decreased yield. The yield at the Savannah River Site was approximately 93%.

Air and moisture needed to be excluded from the pressure vessel reduction systems as buttons prepared in the presence of air and moisture also tended to be pyrophoric. The reduction pressure vessel was heated; the rate of heating was governed by the size of the charge.

Assuming a normal reduction batch of approximately 2,900 g, the dry dried PuF₄/PuO₂ cake could contain up to about 0.8 moles of water. When blended with calcium metal for the reduction step, this sorbed moisture would hydrolyze a portion of the calcium metal. Depending on the amount of water sorbed by the PuF₄/PuO₂ cake, and when the hydrolysis occurred, several undesirable consequences were possible as noted below.

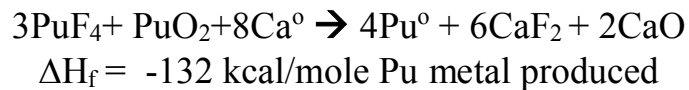
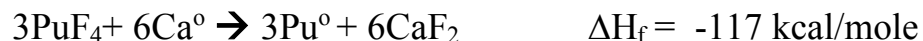
1. Small amounts of moisture coupled with the slow hydrolysis of the calcium metal prior to being sealed in the reduction furnace can lead to:

- Low yields of plutonium metal due to insufficient calcium metal being present for the reduction.
 - Poor coalescence of the plutonium metal due to higher viscosity of the slag and the higher melting point of the slag.
 - Total misfire of the reduction operation.
2. Greater amounts of moisture present two hazards in the reduction process:
- First, the exothermic reaction between calcium metal and moisture in the plutonium powder could, under certain conditions, generate enough heat to initiate the reduction reaction during the handling and mixing operations.
 - Second, at the high temperature reached during reduction, vaporized moisture could pressurize the pressure chamber and expel material from the furnace.

Heating the $\text{PuF}_4\text{-PuO}_2\text{-Ca}^0$ mixture to $\sim 550^\circ\text{C}$ initiates the following exothermic reactions:



Reduction of the cake mixture with theoretical stoichiometry yields the following heats of reaction to the overall heat balance per mole of plutonium metal produced:



The temperature of this calciothermic reaction mixture rapidly rises from about 550°C to about 1500°C .

The melting points of the individual reaction products are:

- CaF_2 $1,418^\circ\text{C}$
- CaO $2,570^\circ\text{C}$

- Pu° 640°C
- CaF₂ (76.5%)-CaO (23.5%) 1,360°C (eutectic mixture)

A phase diagram for the CaF₂-CaO system is shown in Figure 24.XXX.

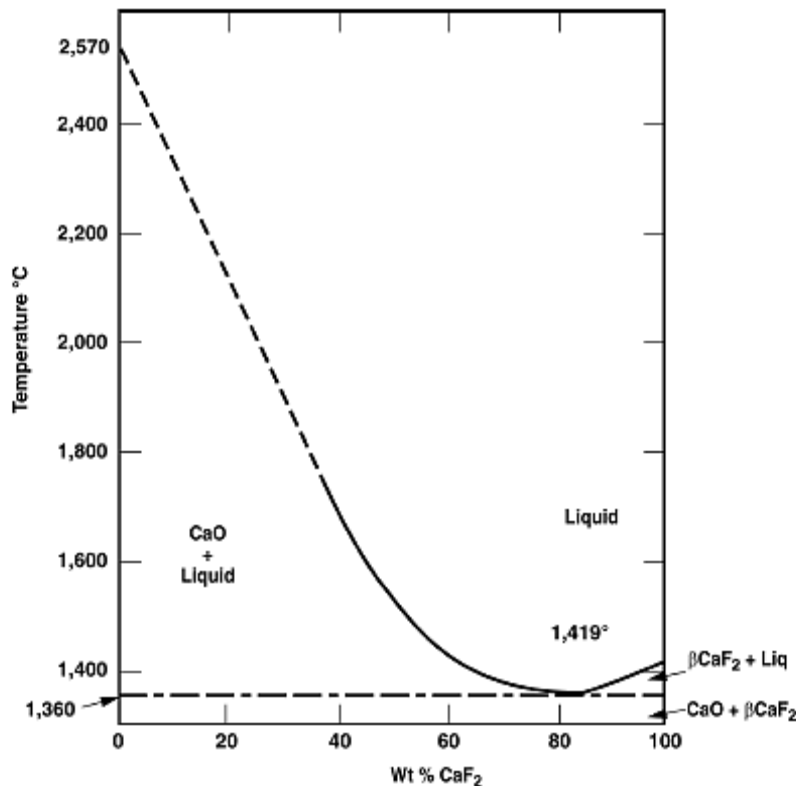


Figure 6-31. CaF₂-CaO system phase diagram.

Concurrent with the rapid temperature rise, there is an immediate decrease in the neutron and secondary gamma radiation levels as the plutonium in PuF₄ is converted to plutonium metal. (Principally, the neutron radiation level is due to the reaction of the plutonium alpha particles on the bonded fluorine atoms to produce neutrons. Therefore, as the reaction proceeds, the resulting plutonium metal is no longer in intimate (i.e., bonded) contact with fluoride atoms, and the plutonium metal coalesces separately from the fluoride in the slag and the neutron levels decrease.)

The success of the reduction operation depends to a large part on the indicated eutectic mixture of fluoride and oxygen that is near the theoretical product of the of the oxygenation operation. Indeed, at the final temperature (~1,500°C), the mixture of reaction products is molten. The fluidity of the CaF₂-CaO mixture allows the more dense plutonium liquid to separate from this mixture and flow

to the bottom of the crucible, forming a button-shaped regulus, and hence the term plutonium button. The CaF_2 -CaO mixture is called slag.

II.F.2.3.3 Button Finishing

As described for the Hanford button finishing in section **II.F.2.3**, the Savannah River Site plutonium buttons were pickled in concentrated HNO_3 to remove the adhering slag, and then rinsed in water to remove the nitric acid.

After water rinsing, the button (Figure 6-32) is allowed to air-dry before it is sampled and packaged.



Figure XXXX. Fresh Plutonium Button

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III. Pyrochemical (Pyrometallurgical) Processes

Development of electrolytic/electrometallurgical technologies ('pyroprocessing') to separate nuclides for spent nuclear fuel reprocessing has been on going by the U.S. Department of Energy National Laboratories, most notably Argonne National Laboratory, as well as by the Korea Atomic Energy Research Institute (KAERI) in conjunction with work on DUPIC (Direct Use of Pressurized Water Reactor Fuel in CANDU Reactors and by Russia. In addition, intensive efforts under way in France, Japan, and the United Kingdom are beginning to show significant progress. However, these processes are at an early stage of development compared with hydrometallurgical processes already operational. There has been particular emphasis on fast reactor spent nuclear fuels. These processes involve a smaller plant than hydrometallurgical/ aqueous processes, and so are well suited to closing the fuel cycle at reactor sites, with the need to store only a small volume of actual fission products as waste. [Nash 2006, WNA 2015]

New fuel cycles such as those for fast neutron reactors (including a lead-cooled reactor) and fused salt reactors, along with the possible advent of accelerator-driven systems, require a new approach to reprocessing. This chapter is focused on electrolytic processes ('pyroprocessing') in a molten salt bath. Pyroprocessing is a generic term for high temperature methods. The term 'electrometallurgical' is also increasingly used to refer to this processing in the United States.

Molten salts – or fused salts – lead to operating conditions that are constraining as high temperatures are required and corrosion effects are common, making identification of appropriate containers quite difficult. Molten salts also have some properties, which make them attractive for nuclear applications:

1. They are less subject to radiolytic degradation than aqueous media due to their ionic liquid structure;
2. Criticality concerns and problems are reduced due to the absence of neutron moderating elements and organic solvents.

These attractive properties, in particular, enable the processing of materials producing high radiation loadings, for example, the high concentrations of fissile materials found in spent nuclear fuels after a short cooling interval. In addition, it is possible to reduce the number of chemical conversion steps compared to those needed for aqueous processes. [Nash 2006] The first significant attempts at actinide metal production in molten salts started with the Manhattan Project in the 1940s [Rhodes, 1986]. Significantly, Kolodney (1982) confirmed that uranium and plutonium could be electrodeposited from molten chlorides. Willit, et al. [Willit et al. (1992)] has reviewed the literature on electrorefining (ER) of

uranium and plutonium in molten salts. Bochco and Skiba [Bychkov and Skiba 1999] have described the basic chemistry and technologies that were developed in Russia. [Nash 2006]

Molten alkali and alkaline earth chlorides have been most extensively studied salt systems for plutonium conversion and separation [Nash 2006]. The basic chemistry and proof of principle were worked out initially for the recovery and purification of plutonium for the plutonium recycle for weapons programs. Three processes are in use throughout the world at significant scale-up [Moser and Navratil, 1983]:

- (i) Direct oxide reduction (DOR) process which consists of PuO_2 reduction by calcium in calcium chloride salt system
- (ii) Molten salt extraction (MSE) process for ^{241}Am removal from weapon-grade plutonium by Mg metal in an alkali chloride salt;
- (iii) ER process for high plutonium purification using molten alkali and/or alkaline earth chloride electrolyte.

Based on the success of these three unit operations, pyroprocessing has also been proposed and is being developed for reducing the cost of fuel fabrication and spent nuclear fuel reprocessing [Motta, 1956]. Between 1964 and 1969, a rudimentary process without molten salts – melt refining – was first demonstrated at Idaho Falls (Argonne National Laboratory West) to recycle metallic fuel from the second experimental breeder reactor (EBR II) [Trice and Chellew, 1961; Stevenson, 1987].

At the same time in the former Union of Soviet Socialist Republics, emerged a concept of vibropacked fuel fabrication for fast reactors and pyroelectrochemical reprocessing based on electrolysis of oxide fuel in molten alkali chlorides. After being applied to uranium oxide spent nuclear fuel, the Dimitrovgrad Dry Process (DDP) process has been adapted today for MOX fuel reprocessing and weapon-grade plutonium conversion into plutonium oxide for civilian use in Russian fast reactors [Bychkov et al., 1995; Skiba and Ivanov, 1995].

A combination of the electrometallurgical technology and a set of molten salt/liquid alloy extractions are now being considered around the world for various fuel cycle concepts. Japan calls for the development of:

- (i) a global fuel cycle combining oxide fuel in pressurized water reactors (PWR) with transmutation of actinides as metal fuel in fast neutron reactors and
- (ii) a ^{15}N enriched nitride fuel cycle involving molten salt reprocessing for ^{15}N

management.

For both projects, spent nuclear fuel reprocessing should take place in a LiCl–KCl melt using previous separation techniques such as the DOR process (lithium substituting for calcium), the ER process with a solid or liquid cathode, and/or the MSE process [Inoue et al., 1991; Arai and Yamashita, 1997; Takano et al., 1998].

Since the mid 1990s, countries of the European Union (Great Britain, France, Spain, Italy), the European Institute for Transuranium Elements (Karlsruhe, Germany), and the Czech Republic have launched research programs for the development of molten salt chemistry and technology for various applications (Partitioning & Transmutation, future fuel cycles). At present, these programs only involve work at the laboratory scale on fundamental aspects or small pilot projects.

Finally, a fused medium in which fuel and reprocessing are strongly connected typically uses molten fluorides. In the past, molten fluorides have been developed as fuel and coolant in molten salt reactor systems. The development for the molten salt breeder reactor concept, using molten LiF–BeF₂ solutions was largely carried out at the Oak Ridge National Laboratory in the 1960s. Today molten salt reactor development has been stopped, although some countries continue isolated investigations (e.g. the Czech Republic or Russia).

Pyroprocessing encompasses several types of material phase including: volatilization; liquid-liquid extraction using immiscible metal-metal phases or metal-salt phases; electrolytic separation in molten salt; and fractional crystallization. They are generally based on the use of either fused salts such as chlorides or fluorides (e.g. LiCl + KCl or LiF + CaF₂) or fused metals such as cadmium, bismuth or aluminum. They are most readily applied to metal rather than oxide spent nuclear fuels, and are envisaged for spent nuclear fuels from Generation IV reactors. Although aqueous systems have played the dominant role in spent nuclear fuel reprocessing, pyrochemical and pyrometallurgical processes are under active development, show great promise, and may find numerous plant-scale applications in the future. These processes are not currently in significant use worldwide. The interest in such processes stems from their considerable advantages [Cleveland 1980] over the more conventional aqueous processes:

- Ability to process fuel after only a short cooling period, since no materials subject to radiation decomposition are present.

- Readily applied to high-burnup spent fuel and require little cooling time, since the operating temperatures are high already.
- Do not use solvents containing hydrogen and carbon, which are neutron moderators creating risk of criticality accidents.
- Reduction in number of chemical conversion steps by elimination of the solid-aqueous solution-solid cycle necessary in aqueous processes.
- Possible recovery of alloying materials.
- Production of fission product waste in a dry, concentrated form more readily stored or processed to recover specific fission products.
- Alleviation of criticality problems in plant design due to the absence of neutron moderating materials, with a consequent reduction in costs.
- Small process equipment required due to reduced volumes; the plant size requirements are typically an order of magnitude smaller than needed for aqueous methods, allowing on-site reprocessing at the reactor site.
- Ability to separate many or even all actinides at once and produce highly radioactive fuel, which is harder to manipulate for theft or making nuclear weapons.
- Most of the radioactivity in roughly 10^2 to 10^5 years after the use of the nuclear fuel is produced by the actinides, since there are no fission products with half-lives in this range. These actinides can fuel fast reactors, so extracting and reusing (fissioning) them reduces the long-term radioactivity of the wastes.
- Alternatively, voloxidation can remove 99% of the tritium from used fuel and recover it in the form of a strong solution suitable for use as a supply of tritium.

While pyrochemical processes have inherent advantages, there are a number of disadvantages. [Nash 2002]

- With one exception (fluoride volatility), pyro-processes have the disadvantage of low decontamination factors, thus requiring remote fabrication of reprocessed fuel. This requirement is not a serious disadvantage in the reprocessing of extensively recycled plutonium fuels, however, the buildup of radioactive heavy isotopes of uranium and plutonium would restrict the direct handling of such fuels even if all the fission products were removed.
- Sophisticated equipment and specialized operating conditions are required.
 - Process temperatures are typically 1100°K.

- Both process reagents and refractory materials used to contain them are susceptible to air oxidation; hence process operations must be carried out in truly inert and dry atmosphere.
- Very high purity reagents must be used. All reagents must dry prior to use.
- Reprocessing as a whole is not currently in favor, and places that do reprocess already have PUREX plants constructed. Consequently, there is little demand for new pyrometallurgical systems and corresponding facilities, although there could be if the Generation IV reactor programs become reality.
- If the goal is to reduce the longevity of spent nuclear fuel in burner reactors, then better recovery rates of the minor actinides need to be achieved.

Since fuel cycle costs are a significant part of reactor operating expenses, successful utilization of a non-aqueous process would be a major step toward the attainment of economically competitive nuclear power. Unfortunately, there are engineering difficulties associated with such systems, and none has received plant application, while most have not progressed beyond the laboratory stage.

Furthermore, many such processes are designed solely to decontaminate uranium rather than to recover plutonium, and their description is beyond the scope of this volume. Consequently, emphasis will be placed on processes that permit plutonium recovery; because many of the processes have only preliminary, unproved status, those processes will be discussed only briefly.

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III.A Volatility Processes

Fluoride volatility processes [Cleveland 1980] utilize the high volatilities of the hexafluorides of plutonium and uranium to separate them from fission products. A typical process would involve the preoxidation of the PuO_2 - UO_2 fuel pellets to convert UO_2 to the more reactive U_3O_8 , followed by a two-stage fluorination of the oxides with a fluorine-oxygen-nitrogen gas mixture in a fluidized bed of fused aluminum oxide (Alundum). (Alundum was chosen for this purpose because its use resulted in the lowest retention of plutonium in the solid residue.) In the first stage, the oxides are fluorinated at 450°C with a gas mixture containing 10 vol.% fluorine; since the U_3O_8 is much more readily fluorinated than PuO_2 , most of the uranium is converted to the hexafluoride and volatilized, at this stage. The remainder of the uranium, along with the plutonium, is removed by heating at 550°C in a gas mixture containing 75 vol.% fluorine. Plutonium removals of 99% or more have been accomplished with this procedure. Other modifications of the process, using different fluorine concentrations and different heating cycles, are also under development.

As mentioned above, a large part of the uranium volatilizes in the first-stage fluorination, thus aiding the uranium-plutonium separation. Further separation of the PuF_6 and UF_6 may be achieved by one of the following methods:

- Fractional distillation, which is based on the difference in volatilities of PuF_6 and UF_6 . In general, two fractions are produced: pure UF_6 and a PuF_6 - UF_6 mixture containing any desired fraction of PuF_6 . As a result, this approach is being considered primarily for fuel cycles that require only an enrichment of the plutonium concentration in the plutonium-uranium

mixture, rather than the complete separation of the two elements. An example of such an application is the recycle of plutonium as mixed $\text{PuO}_2\text{-UO}_2$, which can be prepared directly from the $\text{PuF}_6\text{-UF}_6$ by reaction with a steam-hydrogen mixture.

- Selective chemical reduction of PuF_6 , which is due to its greater reactivity.
- PuF_6 may be reduced to the solid tetrafluoride with SF_4 , elemental bromine and several Freon compounds; Freon-12, employed at 150°C , has been recommended as the preferred compound for this separation. Hydrogen and SO_2 are not suitable, since they also reduce UF_6 under some conditions. Unfortunately, it has been difficult to obtain complete reduction of PuF_6 without some reduction of UF_6 , and the PuF_4 product is a fine powder that might be less readily separated from the gas stream.
- Selective thermal decomposition, which is based on the greater instability of PuF_6 . Trevorrow and coworkers [Trevorrow 1967] have removed 99.5 to 99.970 of the plutonium (as solid PuF_4 containing 0.09 to 1.3% uranium) from a 10:1 $\text{UF}_6\text{-PuF}_6$ mixture by circulating it for as long as 10 hours through heated (200 to 300°C) nickel decomposition vessels packed with nickel wool and containing predeposited PuF_4 . This procedure is therefore the only one that has been proved experimentally on a relatively large scale.
- Selective sorption on beds of MgF_2 , CaF_2 , NaF , or LiF ; which is primarily for the removal of PuF_6 as a trace impurity from a UF_6 stream, since desorption of the PuF_6 is difficult.

Development work has largely been concentrated on fluidized bed processes, but modifications have been studied that involved fluorination and volatilization of plutonium from molten fluoride salts. Recovery of plutonium from molten equimolar NaF-ZrF_4 mixtures and 31-24-45 mole% LiF-NaF-ZrF_4 at 600°C was good, even though the initial concentration of plutonium was only 2 ppm, and similar results were obtained with plutonium concentrations of 1000 ppm. The volatilized PuF_6 was trapped by adsorption on beds of LiF , NaF , or CaF_2 . The reaction rate appeared to be first-order with respect to the plutonium concentration, and was found to have a half-time of about 5.3 hours at 600°C . The long fluorination cycles required as a result of the slow reaction rate result in excessive corrosion, and this problem must be solved before the process can merit serious consideration.

Fluoride volatility [Cleveland 1980] processes have three principal advantages:

- 1) Simplicity.
- 2) High decontamination factors (of the order of 10^8).
- 3) Separation of uranium in the form necessary or gaseous diffusion plant processing.

The processes also have disadvantages:

- 1) More chemical conversion steps than for other pyro-processes (although still less than for aqueous processes).
- 2) The use of fluorine, an expensive reagent.

In the case of UO_2 or mixed PuO_2 - UO_2 processing, however, the fluorine cost may be reduced by preliminary fluorination to PuF_4 and UO_2F_2 with HF , a much cheaper source of fluorine. This approach is under investigation in Europe. In the United States fluorine is less expensive, and since it is the simpler process, employing fluorine as the sole fluorinating agent is preferred.

Present knowledge appears to be sufficient to permit design of a volatility process for uranium recovery, and a combination process involving uranium recovery by volatilization and plutonium recovery by conventional aqueous methods is currently feasible. Such a scheme would require two types of process equipment and would lack the advantage of simplicity possessed by the all-volatility process, but with the uranium removed, the aqueous plutonium recovery operations could be accomplished in small-size equipment.

(b) Metal Volatilization. The higher vapor pressure of plutonium compared to uranium at 1500 to 1800°C makes it possible to separate the two elements by vacuum volatilization [Cleveland 1980]. Unfortunately, most of the rare-earth fission products have vapor pressures in the same range as plutonium, thus necessitating decontamination of the plutonium by a supplementary process. For this reason, metal volatilization has little to recommend it as a plutonium recovery process.

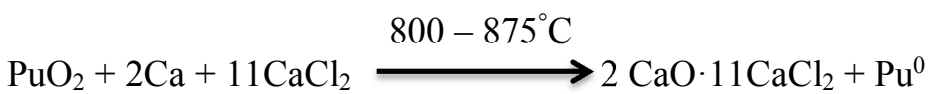
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III.B Direct Oxide Reduction

The Direct Oxide Reduction (DOR) process has been used to produce metal from a variety of feedstocks in both research and development studies as well as in production. [Long 1978, Baldwin 1983, Coops 1983, Wade 1969, Felt 1969, Mosley 1970, Mullins 1982, Mullins 1983, Christensen 1983] The reduction of PuO_2 to metal by calcium is carried out in a CaCl_2 solvent. A mixture of CaCl_2 - CaF_2 can also be used. The reaction, typically carried out at about 850°C , is



$$\Delta H_{1100^\circ\text{K}} = 52 \text{ kcal/mole PuO}_2$$

The salt provides at least two important functions:

1. Calcium metal is soluble in the molten salt; this solubility provides a mechanism for transfer of calcium metal to the PuO_2 for the reduction reaction to occur;
2. Calcium oxide is soluble in the molten salt; this solubility provides a mechanism for separation of CaO from the reduced metal as it coalesces to the bottom of the crucible.

Plutonium metal and PuO_2 are insoluble in the CaCl_2 - CaO - Ca flux; as a result, the plutonium metal consolidates into a molten mass.

Vigorous stirring is necessary to keep the reactants in intimate contact so that the reaction is driven to completion. Upon cooling to room temperature, a well-consolidated plutonium product is obtained at better than 98% recovery.

The reaction is carried out under an inert atmosphere in an open crucible. Vitrified magnesium oxide ceramic is commonly used as a container material, but tungsten and tantalum can also be used. If the latter are used, CaF_2 is added to lower the temperature needed to liquefy the flux, thereby decreasing the corrosion of the crucible and subsequent contamination of the metal product.

Molten calcium metal is a very strong reducing agent at the temperature necessary for these materials to be molten. Therefore, all trapped impurities in the plutonium oxide, CaCl_2 salt, and the calcium metal become a portion of the plutonium metal product. In general, plutonium oxide whose plutonium assay

was less than 85wt.% (~3.2% impurities) would not produce a reasonable yield of acceptable material for feed to ER Process for purification and subsequent feed for weapons.

A more complete discussion of DOR is given in the Pyrochemical Processing chapter.

Researchers in the United States recently have proposed a baseline flowsheet combining aqueous and pyrochemical processes in the framework of the preparation of a technology development roadmap for the accelerator transmutation of waste (ATW) technology (ATW Separations, 1999). From light water reactor (LWR) spent nuclear fuel, the process begins with an aqueous **Uranium Extraction** (UREX) process that would produce a pure uranium stream for waste, technetium, and iodine streams for target fabrication, and a transuranium element–fission product oxide stream. Using pyroprocessing, this oxide stream would be treated for converting transuranic elements into a metallic form suitable for fabrication of ATW fuel (based on Zr). The pyroprocessing should involve two steps: (i) DOR process with lithium metal in a LiCl melt to reduce the actinide oxides to the metallic form and (ii) electrometallurgical technology in a LiCl–KCl melt to separate transuranium elements from the remaining fission products. The baseline option for ATW irradiated fuel processing would use a chloride volatility process for zirconium separation coupled to an electrowinning process in LiCl–KCl for separation of transuranic elements from fission products. [Nash 2006]

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III.C Plutonium Electrorefining

Electrorefining can be used either to purify plutonium metal or process high burn-up fuel, which has had little cooling time.

III.C.1 Purification of plutonium metal via Electrorefining

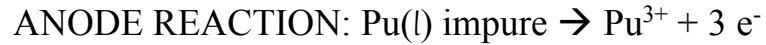
The principle of the ER process is simple [Coops 1983, Baldwin 1983, Christensen 1983, Leary 1958, Mullins 1960, Mullins 1965, Mullins 1982]:

- Impure plutonium metal is oxidized at a liquid metal anode to Pu(III) ;
- Pu(III) ions are transported through a molten salt to the cathode;
- Pu(III) ions are reduced at the cathode to pure plutonium metal.

The transport salt is typically a eutectic salt such as KCl-NaCl . As liquid metal builds up on the cathode it drips off into an annulus where it coalesces into a

pool of liquid metal and is recovered after the cell has cooled to room temperature. The entire process is typically performed in a molten salt bath.

A schematic representation of a typical electrorefining cell is shown in Figure XXXX. The basic chemistry of the electrorefining technique is:



Metallic impurities are either more electropositive or less electropositive than plutonium. Impurities more electropositive than the liquid plutonium anode will be oxidized by Pu^{3+} and be taken up by the salt phase while impurities less electropositive than plutonium will be reduced by plutonium metal and be collected in the anode. [Coops 1983]

To prevent the passage of impurities, the back EMF of the cell is monitored. When the back-EMF reaches a predetermined value, operation of the cell is terminated, and the cell allowed to cool to room temperature. The cathode product, a very pure plutonium metal is recovered from the solidified salt mass by breaking the ceramic vessel and brushing the plutonium free of adhering salt. [Coops 1983]

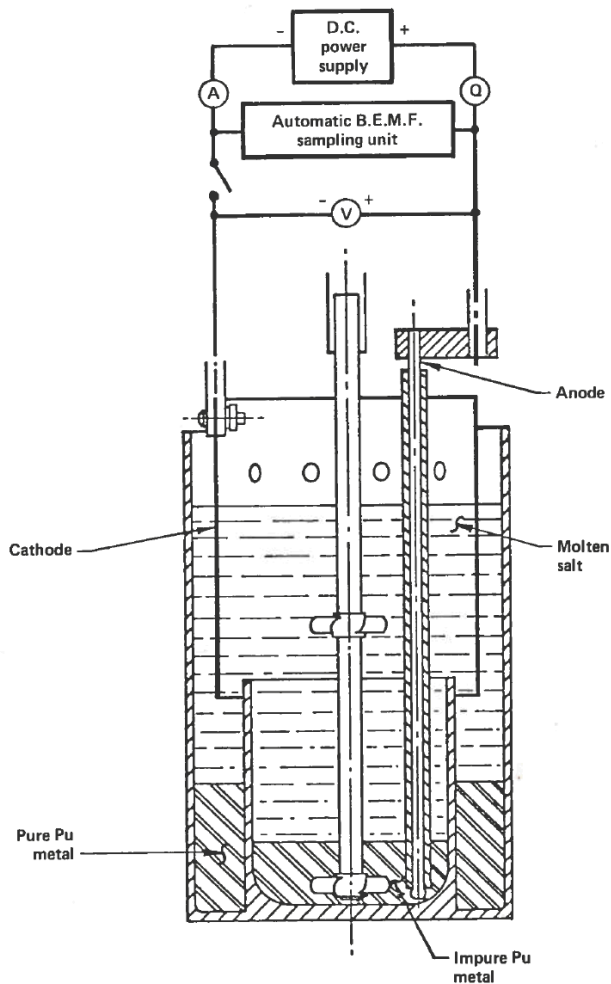


Figure 11. Schematic of Electrorefining Cell Showing Major Features.

A more complete discussion of electrorefining for purification of plutonium metal can be found in the Pyrochemical Processing Chapter.

III.C.2 Electrorefining of Fuels

There has been little research and development related to the application of ER techniques to the recovery and purification of spent nuclear fuels. As a result such processes are at an early stage of development compared with hydrometallurgical processes already operational. However, interest in ER was revived with the proposed advanced fast reactor concept called the integral fast reactor (IFR) [Burris, 1986; Till and Chang, 1988; Chang, 1989; Hannum, 1997] whose primary feature was an integral fuel cycle in which the core and blanket

materials after discharging are to be processed and refabricated in an onsite facility. The fuel cycle was based on electrorefining with a molten salt electrolyte ($\text{LiCl-KCl-UCl}_3/\text{PuCl}_3$) at 500°C in an inert atmosphere. This process has the advantage that it can readily be applied to high burn-up fuel and fuel which has had little cooling time, since the operating temperatures are already high.

Separating (partitioning) the actinides contained in a fused salt bath is by electrodeposition on a cathode, which involves all the positive ions without the possibility of chemical separation of heavy elements such as in the PUREX Process and its derivatives. This cathode product can then be used in a fast reactor.

So far only one electrometallurgical technology has been licensed for use on a significant scale. This is the IFR (integral fast reactor) electrolytic process developed by Argonne National Laboratory in the United States and used pyroprocessing technology for the spent nuclear fuel from the EBR-II experimental fast reactor, which ran from 1963-1994. This application is essentially a partitioning-conditioning process, because neither plutonium nor other transuranics are recovered for recycle. The pyro-process is used to facilitate the disposal of a spent nuclear fuel that could not otherwise be sent directly to a geologic repository. The spent uranium metal fuel is dissolved in a $\text{LiCl} + \text{KCl}$ molten bath, the uranium is deposited on a solid cathode, while the stainless steel cladding and noble metal fission products remain in the salt, and are consolidated to form a durable metallic waste. The transuranic elements and fission products in salt are then incorporated into a zeolite matrix, which is hot pressed into a ceramic composite waste. The highly enriched uranium recovered from the EBR-II driver fuel is down-blended to less than 20% enrichment and stored for possible future use.

GE Hitachi is designing an Advanced Recycling Centre (ARC) that integrates electrometallurgical processing with its PRISM (Power Reactor Innovative Small Module) fast reactors. The main feed is spent nuclear fuel from light water reactors, and the three products are fission products, uranium, and transuranic elements (neptunium, plutonium, americium, and curium), which become fuel for the fast reactors (with some of the uranium). The uranium can be re-enriched or used as fuel for CANDU reactors. As the cladding reaches its exposure limits, spent PRISM fuel is recycled after removal of fission products. A full commercial-scale ARC would comprise an electrometallurgical plant and three power blocks of 622 MWe each (six 311 MWe reactor modules), but a "full-

scale building block" of ARC is a 50 tonnes/year electrometallurgical plant coupled to one 311 MWe reactor module, with breeding ratio of 0.8.

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III.D Slagging Processes

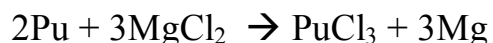
III.D .1 Halide Slagging (Molten Salt Extraction)

Mullins et al, [Coops et-al 1983, Mullins et-al 1962], at the Los Alamos National Laboratory, demonstrated that americium could be partitioned between molten plutonium metal and a molten NaCl-KCl salt containing Pu(III) ions; Knighton et-al, [Coops et-al 1983, Knighton et-al 1965] working at the Argonne National

Laboratory on molten salt separation processes for fuel reprocessing, demonstrated that the americium could be extracted from Mg-Zn-Pu-Am alloys with immiscible magnesium chloride. Long et al. [Coops et al. 1983, Long et al. 1962] at the Rocky Flats Plant initiated work to study the extraction of americium from molten plutonium using molten NaCl-KCl salt containing a few percent MgCl₂. A production process evolved for this for use at Rocky Flats. The basic chemistry is covered in the chapter on Pyrochemical Processing.

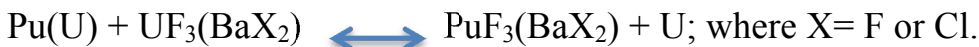
It is feasible to selectively extract highly electropositive fission product elements, such as the rare earths, alkali, and alkaline earth elements selectively from molten uranium-plutonium-fissium alloys***** into an overlying molten halide salt layer or flux. The process, which is of the melt refining type, is called halide slagging. The attractive features are the short operating time (about one hour at temperature), relatively low operating temperature (~1150°C), and a high product yield (>96%).

In the halide slagging process, in particular chloride slagging, the active fission products were rapidly removed from the molten fuel as a result of chemical reactions occurring at the interface between two liquid phases. Moreover, the plutonium transfer was less than 1 wt%. The process consisted of contacting the molten fuel at 600–700°C with molten alkali chloride salts containing plutonium trichloride or magnesium chloride as an oxidant:



Tested slags were PuCl₃–NaCl, MgCl₂–LiCl-KCl, or MgCl₂–NaCl–KCl (Leary et al., 1958; Mullins et al., 1960).

Plutonium may be extracted from molten uranium by contacting it with molten UF₄-BaCl₂ (or BaF₂), the latter serving to lower the melting point of the salt phase. UF₃, formed by reduction of the tetrafluoride by uranium metal, oxidizes the plutonium to form the trifluoride, which extracts into the salt phase



On a mole fraction basis, the equilibrium constant for this reaction at 1200°C was found to be 72 ± 36 . McKenzie et al. [McKenzie 1958] found that over

***** Fissium alloys was coined by ANL to indicate the mixture of fission products

90% of the plutonium was extracted into molten UCl_3 or MgCl_2 in a single contact. Under optimum conditions molten barium halides alone may also be used to extract plutonium from uranium at 1200 to 1350°C, the extraction improving with time due to vaporization of barium.

Because of their electropositivity, alkali, alkaline earth, and rare-earth fission products follow the plutonium into the salt phase, from which an additional process to purify the plutonium must be used to remove those fission products. If the plutonium product is converted to metal by bomb reduction with calcium, the bulk of the rare-earth fission products report to the reduction slag.

Laboratory studies have indicated that cerium (used as a stand-in for all electropositive fission products) may be efficiently extracted from a molten 10 wt % uranium-10 wt% plutonium- fission (cerium) alloy by contacting with a 19 wt% CaCl_2 -81 wt% BaCl_2 flux (with a flux/metal ratio of about 2:7) containing MgCl_2 for one hour at 1150°C. The concentration of MgCl_2 must be controlled within rough limits to avoid extraction of plutonium. When 110% of the stoichiometric amount of MgCl_2 necessary to oxidize all the cerium to CeCl_3 was used, 98% of the cerium was removed along with less than 0.5% of the plutonium, giving a cerium-plutonium separation factor of approximately 7000; but a 100% excess of MgCl_2 increased the plutonium extraction to about 2% and the cerium removal to about 99%. Since the amount of fission products formed can be determined by analysis or calculation, however, it is not difficult to estimate the proper amount of MgCl_2 to use in the flux.

A process being studied involves dissolving irradiated uranium in molten zinc followed by extracting the uranium, plutonium, and more electropositive fission products into a molten chloride salt phase containing ZnCl_2 . The noble metal fission products are left in the zinc, which is discarded. The uranium and plutonium are then extracted into a cadmium-zinc-magnesium alloy, the magnesium functioning as the reducing agent. (MgCl_2 in the salt phase is the oxidizing agent.) Plutonium and uranium are recovered from the alloy by vacuum distillation of the solvent metals. The available data suggest that four extraction stages should remove 95% of the fission products with plutonium and uranium recoveries of 99%. Cadmium is included in the alloy phase to lower the melting point and corrosion sufficiently to permit the use of stainless steel, rather than refractory metal, containers.

Apparently the slag solvent composition is of minor importance, provided that it is made up of stable halide compounds and has a sufficiently low melting point.

Presumably compounds such as lithium, sodium, potassium, calcium and barium chlorides can be used. Therefore the melting point of the slag can be varied over a reasonably wide range. [Mullins 1960]

Although the above procedures refer to metallic fuels, it apparently can be adapted to oxide and carbide fuels as well. The EBR-II skull recovery process to remove noble metal impurities and convert the uranium and plutonium oxides to metal, which would be processed by using MSE, could treat oxide fuels. Carbide fuels could be converted to the oxides and processed similarly. Alternately, carbides could be converted to chlorides in molten salt solution or to the metals in molten zinc.

Leary *et al.* [Leary 1958] have also investigated halide slagging as a process for removing fission products from irradiated plutonium fuels. By use of a PuCl_3 - NaCl eutectic at 600°C , they were able to extract rare-earth elements into the salt phase, while the more noble metals (i.e., ruthenium and molybdenum) remained in the molten metal phase. It was also possible to use MgCl_2 instead of PuCl_3 as the oxidant. Plutonium extraction was less than 1% if the amount of MgCl_2 was limited to 110% of the stoichiometric amount necessary to oxidize the rare-earth elements.

Halide slagging processes are thus not well suited for general use, but they have been considered as complementary to various other proposed processes, such as mercury recrystallization and liquidation. If favorable equilibrium constants are found, salt slagging may prove useful for the extraction of plutonium from fast breeder reactor blanket material. [Vogel 1965]

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III.D .2 Molten Metal-Molten Salt Extraction Processes

By combining liquid metal (or alloy) solvent with molten salts and using oxidation–reduction reactions, it is possible to accomplish separations that could not be achievable by melt refining [Cleveland 1980, Nash 2006]. The elements are distributed in the two-phase solvent system (molten metal/molten salt) and the distribution coefficients depend on the nature of the oxidizing and reducing agents and on the activities of the reacting species in solution. In general, chlorides are preferred because of their lower volatility, their compatibility with many containers, and favorable solubility relationships. Such separation techniques in various biphasic systems have been proposed in the past by several U. S. laboratories: Brookhaven National Laboratory investigated Bi/MgCl₂–NaCl–KCl to reprocess bismuth–uranium fuel (Bennett et al., 1964); the Hanford Works studied the actinide distribution in Al/AlCl₃– KCl (Dwyer, 1956); the Ames Laboratory examined the same in Zn/LiCl–KCl (Moore and

Lyon, 1959); the Los Alamos National Laboratory tested Hg/RbCl–LiCl–FeCl₂ for the reprocessing of Los Alamos Molten Plutonium Reactor Experiment (LAMPRE) fuel (Chiotti and Parry, 1962); the Argonne National Laboratory proposed various applications in MgCl₂–based salt with Cu–Mg or Zn–Mg alloy. One of them is the Argonne salt transport process for the reprocessing of Liquid Metal Fast Breeder Reactor (LMFBR) fuels (Steunenberg et al., 1970)

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III.D .3 Oxide Slagging or Melt Refining

Between 1964 and 1969, a rudimentary process without molten salts – melt refining – was first demonstrated at Idaho Falls by the Argonne National Laboratory West to recycle metallic fuel from the second experimental breeder reactor (EBR-II) [Trice and Chellew, 1961; Stevenson, 1987, Motta, 1956; Burris et al., 1964]. Melt refining is also named oxide slagging or oxide drossing. Fission products are removed by combining volatilization and selective oxidation. The fuel is melted in a lime-stabilized zirconia crucible and held in a molten state at 1400°C for 1 to 3 hours under an inert atmosphere, after which the molten metal is poured away from the dross. About 25% of the expected fission products, namely those with high vapor pressures (such as krypton, xenon, cesium, cadmium, and iodine), are removed by volatilization. The alkaline earth and rare earth elements (comprising about 40% of the fission products), whose oxides are more stable than plutonium and uranium oxides, react with the oxygen of the zirconia crucible to form a dross, or slag, that adheres to the crucible surface. In experiments with highly-irradiated fuel, the following fission product removals (in %) were obtained: cesium, strontium, barium, and iodine, 99+; rare earths and yttrium, 97 to 99+; tellurium, 95 to 99+; zirconium, 9 to 28; molybdenum and ruthenium, 0. Zirconium, constituting about 10% of the fission products, may be removed into the dross as insoluble zirconium carbide by the addition of finely divided carbon to the melt (carbide slagging), or it can be removed during skull recovery.

Not removed from the melt by the above procedures are other noble and refractory metal fission products (technetium, silver, rhodium, tin, and palladium), which remain with the molten metal when it is poured from the crucible. To avoid buildup of these elements, a portion of the fuel is withdrawn during each cycle and processed by a separate procedure.

The skull remaining in the crucible contains 5 to 10% of the original charge, as well as the dross consisting of fission product oxides. In addition, there is a small preferential concentration of plutonium in the skull. Thus it is necessary

that the skull be recovered by another processing method, based on selective extraction and reduction from a flux of alkaline earth halides into molten zinc and zinc-magnesium alloys. The skull reclamation process does not permit recovery of plutonium. The melt refining process has the advantage of simplicity, but appears to be limited to the processing of metallic fuels containing less than 20 wt.% plutonium. In addition, the need to process the skull and a portion of the refined metal by alternate processes is a definite drawback.

This process has been demonstrated on a larger scale with enriched uranium fuel from EBR-II. The ultimate success of the EBR-II close-coupled process would undoubtedly have a great influence on future pyrometallurgical process development.

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III.D .4 Carbide Slagging

Addition of carbon (either as finely-divided powder or in the form of a graphite rod) has been investigated as a means of removing zirconium from molten metal systems by forming the insoluble carbide. This technique has had some success in the melt refining process; for processing an experimental plutonium-iron alloy fuel, however, addition of carbon reduced the plutonium yield without achieving adequate zirconium decontamination.

III.D .4 .1 Liquid Metal Processes

- (a) Processing of Melt Refining Skulls. The recovery of plutonium from skulls from the melt refining of EBR-II fuels is to be accomplished by a tentative process involving oxidation of the skull to the respective oxides, which are then suspended in a molten $\text{MgCl}_2\text{-CaCl}_2\text{-MgF}$ flux and vigorously contacted with molten zinc to extract fission product ruthenium, rhodium, palladium, molybdenum, and technetium (to achieve adequate ruthenium removal, it is apparently necessary to add a small

amount of oxidant, such as ZnCl_2 , to the flux.) The plutonium, uranium, and fission product oxides are then reduced at 800°C with molten zinc-5% magnesium alloy, after which the plutonium and uranium are precipitated from the flux in two successive steps: first, by cooling the melt to about 500°C and then by the addition of more magnesium to lower the uranium solubility. The precipitates are then retorted at 600 to 850°C to remove magnesium and zinc. The process has been demonstrated on a pilot-plant scale to achieve good removal of fission products. It is not applicable to plutonium bearing fuels, however, since it does not achieve a separation of plutonium from rare-earth fission products.

(b) Processing of EBR-II Blanket Material. The plutonium in the irradiated natural uranium blanket of EBR-II must be increased in concentration from 1% to at least 40% before it can be used to enrich other core loadings. This concentration is accomplished by a process based on the differing solubilities of the two elements in magnesium-zinc solutions of varying compositions. The plutonium-uranium alloy is dissolved at 800°C in zinc containing 12 to 14% magnesium to produce a solution containing 12 to 14% uranium. Addition of magnesium (to a concentration of 50%) and cooling to about 400°C results in the precipitation of most of the uranium due to its low solubility in magnesium-rich zinc alloys. The plutonium and part of the uranium remain in the alloy phase; their respective concentrations are 0.08 and 0.04%. The plutonium concentration is increased to 1 to 10% by evaporation of most of the zinc and magnesium. This concentrated solution is then fed into the main core fuel cycle to enrich the fuel. The process has been demonstrated on a laboratory scale with the product having a plutonium concentration of between 44 and 70%.

(c) Molten Metal Extraction. Plutonium may be removed from molten uranium by extracting it into an immiscible metal, such as silver, silver-gold alloy, or magnesium. Silver, for example, was found to be an efficient extractant; the extraction coefficient for plutonium from molten uranium containing 0.2% plutonium into silver was found to be 14 ± 1 , with equilibrium being attained in 20 min. From uranium containing 0.0018% plutonium the extraction coefficient was two. Unfortunately, most of the fission products also extract thus requiring that the plutonium be processed further before reuse. Furthermore, molten metal extraction processes suffer from the difficulties of obtaining good metal-metal contact at high temperatures, from mutual solubility effects which

interfere with efficient separation and recovery of uranium and plutonium, and from unfavorable physical properties-such as vapor pressures that are too high or too low-of the extractant metals. For these reasons, molten metal extraction processes have little merit and have received no serious consideration.

- (d) Recrystallization from Mercury. The large variation in solubility of plutonium in mercury as a function of temperature is the basis of a proposed process for the recovery of plutonium from an experimental plutonium iron alloy fuel. The procedure calls for the dissolution of plutonium iron alloy in mercury at 325°C and contacting this solution with a RbCl-LiCl-FeCl₂ salt phase to remove rare earths by the reaction



The resulting rare earth salts extract into the slag. The mercury is filtered at 300°C to remove the slag and other insoluble materials, after which it is cooled to 25°C to recrystallize a plutonium-mercury intermetallic compound (probably PuHg₄). The latter is removed by filtration and retorted *in vacuo* at 750°C to volatilize the mercury. The resulting plutonium is sufficiently free of fission products for reuse. The process is currently in disfavor, however, largely due to undesirable properties of the plutonium-mercury intermetallic compound:

- It is pasty and difficult to filter.
- It is highly pyrophoric, thus requiring that processing be conducted in an inert atmosphere.

Because of these disadvantages, large-scale application of the mercury recrystallization process appears unlikely.

(e) Precipitation from Calcium-Zinc Solution. By taking advantage of the high solubilities of the rare earths, and the low solubilities of plutonium and uranium in calcium, it is possible to effect a separation. The plutonium-uranium metallic fuel may be dissolved in molten zinc and the plutonium and uranium precipitated by the addition of calcium. Unfortunately, the solubility of plutonium in the zinc-calcium is not low enough to prevent appreciable loss of plutonium in the supernate, and therefore the value of the procedure is dubious.

(f) Metal Liquefaction. If a fission product is present in an irradiated fuel in

an amount exceeding its solubility, it should be possible to remove it by holding the fuel in the molten state. This procedure, known as liquation, has been investigated as a method for removing relatively noble fission products from irradiated plutonium fuels. By holding synthetic plutonium-iron-fissium alloys at 600°C for about 22 hours and then filtering rapidly through a graphite filter, it was possible to remove most of the fission product zirconium, molybdenum, niobium, and lanthanum. The ruthenium concentration was not altered significantly, and only about 20% of the cerium was removed. Combined with halide slagging, liquation may be a feasible interim process to allow higher burnups to be achieved before buildup of soluble fission products requires more elaborate processing. The results also indicate the necessity for filtering molten reactor fuels periodically to prevent the formation of insoluble fission product deposits in the reactor core.

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28.xxxxx Electrolytic Processes.

(a) Metal Electrolysis. Preliminary experiments suggest that electrolysis may be a feasible method for reprocessing irradiated plutonium fuels. In laboratory runs with a synthetic plutonium-iron-fissium alloy, the synthetic alloy was the anode in a cell containing an iron cathode and a molten salt electrolyte consisting of LiCl, KCl, and PuCl₃. Electrolysis at 550° C at a potential of 1 volt produced a cathode pool of molten plutonium that had been efficiently decontaminated from typical rare earth and noble metal fission products. The rare earths concentrated in the salt phase, while elements such as ruthenium, molybdenum, and zirconium remained in the anode sludge. Such electrolytic procedures have the advantages of simplicity and adaptability to continuous processing and appear promising for future plant-scale operations. At present, however, they are in a

relatively early stage of development.

(b) The Salt Cycle Process. The Salt Cycle Process is under development for reprocessing $\text{UO}_2\text{-PuO}_2$ fuels, such as those from the Plutonium Recycle Test Reactor (PRTR). The conceptual process involves dissolution of the spent nuclear oxide fuel in a molten LiCl-KCl mixture while sparging with chlorine or, preferably, a mixture of hydrochloric acid and chlorine, followed by the electrodeposition of PuO_2 and UO_2 on a graphite electrode. Operating conditions depend on the nature of the spent nuclear fuel to be processed and on the type of product desired.

For processing highly-enriched UO_2 , if plutonium recovery is not necessary, the oxide is dissolved in an equimolar LiCl-KCl mixture with chlorine sparging; the resulting UO_2Cl_2 is electroreduced at 550 to 800°C to UO_2 and deposited on the cathode, leaving plutonium and rare-earth fission products in the melt. If recovery of both UO_2 , and PuO_2 is desired, the oxide is dissolved in an equimolar LiCl-KCl mixture, again with chlorine sparging, after which the melt is electrolyzed at 475 to 675°C, while being sparged with an oxygen-chlorine mixture, to deposit a $\text{PuO}_2\text{-UO}_2$ solid solution on the cathode. Dense crystalline deposits have been prepared containing from 1 to 35% PuO_2 in UO_2 and enriched in plutonium (compared to the melt) by factors of 1 to 40, the enrichment depending on oxygen concentration in the sparge gas (high oxygen content favors greater plutonium enrichment), temperature, current density, and fraction of the total uranium deposited. Recovery of PuO_2 from $\text{UO}_2\text{-PuO}_2$ mixtures, this may be accomplished by dissolving the material in a 2.5:1 LiCl-KCl mixture with chlorine sparging, and then sparging the melt at 550°C with an equimolar mixture of oxygen and chlorine, without electrolysis, to precipitate crystalline PuO_2 . Decontamination factors of about 500 for uranium and 100 to 200 for rare-earth fission products are obtained in the PuO_2 precipitation process, while the electrolytic co-deposition of $\text{PuO}_2\text{-UO}_2$ solid solutions achieves rare-earth decontamination factors of only 3 to 25 (relative to plutonium); in both cases decontamination from zirconium and cerium is poor.

The Salt Cycle Process has been tested on a laboratory scale with both plutonium and uranium oxides, and on a pilot-plant scale with UO_2 . In addition, hot cell tests using irradiated PRTR fuel elements have been conducted. Although the results have been moderately encouraging, the low decontamination limits the value of this process.

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III.E Pyro-Processing Development at various Laboratories

III.E .1 Argonne National Laboratory

The Argonne National Laboratory development of reprocessing for the spent nuclear fuel from its integral fast reactor, EBR-II, was presented in Section III.C.2 in this chapter.

III.E .2 Idaho National Laboratory

The PYRO-A process, being developed at the Argonne National Laboratory West to follow the UREX Process, is a pyrochemical process for the separation of transuranic elements and fission products contained in the oxide powder resulting from denitration of the UREX Process raffinate. The nitrates in the residual raffinate acid solution are converted to oxides, which are then subjected to an electric current in a LiCl-Li₂O molten salt bath. The more chemically

active fission products (e.g., cesium, strontium) are not reduced and remain in the salt. The transuranic oxides are reduced to a metal and collect on a solid cathode. The salt bearing the separated fission products is then mixed with a zeolite to immobilize the fission products in a ceramic composite waste form. The cathode deposit of transuranic elements is then processed to remove any adhering salt and is formed into ingots for subsequent fabrication of transmutation targets.

The PYRO-B process has been developed for the processing and recycle of spent nuclear fuel from a transmuted (fast) reactor. A typical transmuted fuel is free of uranium and contains recovered transuranics in an inert matrix such as metallic zirconium. In the PYRO-B processing of such fuel, an ER step is used to separate the residual transuranic elements from the fission products and recycle the transuranics to the reactor for fissioning. Newly generated technetium and iodine are extracted for incorporation into transmutation targets, and the other fission products are sent to waste.

III.E .3 Russian Institute of Atomic Reactors (RIAR)

Russian pyroprocessing consists of three main stages: dissolution of the used nuclear fuel in molten salts, precipitation of PuO_2 or electrolytic deposition of UO_2 and PuO_2 from the melt, then processing the material deposited on the cathode or precipitated at the bottom of the melt for granulated fuel production. The process recovers the cathode deposits without changing their chemical composition or redistributing the plutonium. All spent nuclear fuel is reprocessed with the goal of having a complete recycle of plutonium, neptunium, americium, and curium as well as the uranium. This process, combined with vibropacking⁺⁺⁺⁺⁺ in fuel fabrication will be used to produce fuel for the BN-800 fast reactor. The technologies complement one another well and involve high levels of radioactivity throughout, making them self-protecting against

+++++ Vibropacked MOX fuel (VMOX) is seen as the way forward. This fuel is made by agitating a mechanical mixture of UO_2/PuO_2 granulate and uranium powder, which binds up excess oxygen and some other gases (that is, operates as a getter) and is added to the fuel mixture in proportion during agitation. The getter resolves problems arising from fuel-cladding chemical interactions. The granules are crushed UPuO_2 cathode deposits from pyroprocessing. VMOX needs to be made in hot cells. It has been used in BOR-60 since 1981 (with 20-28% Pu), and tested in BN-350 and BN-600.

diversion or misuse.

The Russian Institute of Atomic Reactors (RIAR) at Dimitrovgrad has developed a pilot scale pyroprocessing demonstration facility for fast reactor fuel.

III.E .4 Korean Atomic Energy Institute (KAERI)

The KAERI advanced spent nuclear fuel conditioning process (ACP) involves separating uranium, transuranics including plutonium, and fission products including lanthanides. It utilizes a high-temperature lithium-potassium chloride bath from which uranium is recovered electrolytically to concentrate the actinides, which are then removed together (with some remaining fission products). The latter product is then fabricated into fast reactor fuel without further treatment. The process is intrinsically proliferation-resistant because it is so hot radiologically, and the curium provides a high level of spontaneous neutrons. The KAERI recycles about 95% of the spent nuclear fuel.

Development of this process is at the heart of the nuclear cooperation between the United States and the Republic of Korea (South Korea), and is central to the renewal of the bilateral U.S.-South Korean nuclear cooperation agreement in March 2014, so is already receiving considerable attention in negotiations.

With U.S. assistance through the International Nuclear Energy Research Initiative (I-NERI) program, KAERI built the Advanced Spent Fuel Conditioning Process Facility (ACPF) at KAERI. Demonstration work is proceeding to 2016, as effectively the first stage of a Korea Advanced Pyroprocessing Facility (KAPF) to start experimentally in 2016 and become a commercial-scale demonstration plant in 2025.

South Korea has declined an approach from China to cooperate on electrolytic reprocessing; Japan's Central Research Institute of Electric Power Industry (CRIEPI),^{*****} due to government policy, has also been rebuffed China.

III.E .5 Japan

Development of pyrochemical technologies for irradiated fuel processing in Japan is being pursued by three separate entities: the Central Research Institute

^{*****} CRIEPI is an acronym that stands for Central Research Institute of Electric Power Industry

of Electric Power Industry (CRIEPI), the Japan Atomic Energy Research Institute (JAERI), and the Japan Nuclear Cycle Development Institute (JNC).

JAERI does not have a long history of pyrochemical study for partitioning and transmutation (P&T) schemes. Electrorefining of nitride fuel in LiCl-KCl molten salt was started in the mid-1990s in a co-operation with CRIEPI. High-purity argon gas-atmosphere glove boxes for pyrochemical studies were manufactured; two electrorefiners and one cathode processor were installed in the glove boxes. Experiments with 10 g material inventories are under way using uranium, neptunium, and plutonium.

The Japan Nuclear Cycle Development Institute (JNC) is leading a feasibility study (FS) in Japan concerning the development of a commercialized fast reactor and its associated fuel cycle system.

CRIEPI aims at optimizing operating conditions for the use of electrorefining methods. For instance, experiments on the reduction of UO_2 , carried out in co-operation with Kyoto University, have confirmed that more than 99% of the UO_2 was converted into metallic form. Feasibility has been confirmed using UO_2 .

Central Research Institute of Electric Power Industry (CRIEPI) pyrochemical process consists of the following steps:

1. Voloxidation of oxide fuels
2. Electrowinning of UO_2
3. Reduction of remaining actinide oxides to metal
4. Separating the reduced metal by ER
5. Removing salt and cadmium from the cathode by distillation

What is unique about the CRIEPI process is using oxide electrowinning before reduction to reduce the amount of fuel processing [Inoue, 2011]. This approach reduces cost and facility footprint.

There have been a series of experiments completed to optimize the flowsheet parameters. First, UO_2 recovery has been demonstrated by electrowinning in a LiCl-KCl molten salt, [Kurata, 2005]. Also, the performance of the reduction operation to the ER step has been demonstrated with uranium and plutonium oxide and MOX fuel. In particular, the overall material balance was verified and the anode residue was calculated and matched to experimental data [Koyama, 2007]. Further testing has demonstrated the ability to recovery actinides from the anode residue using K_2LiCl_4 as an oxidizing agent [Kurata, 2006]. Actinides are further recovered with high yield from the molten salt phase using a multi-step

reduction process. This step is operated to promote a separation of the actinides from lanthanides. Validation work included thermodynamic calculations that compared well with experimental data [Kinoshita, 1999]. In summary, material balances for several different variants of the flowsheet are still under development for different types of fuel. The composition of products from four different fuel compositions is shown below in Table XX-X.

Table XX-X. Product Compositions from CRIEPI Pyro-process

Spent Fuel	Uranium (wt %)	Plutonium (wt %)	Minor Actinides (wt%)	Lanthanides (wt%)
UO ₂ , 45 GWd/t	46.5	46.5	4.6	2.3
UO ₂ , 60 GWd/t	45.7	45.7	5.9	2.7
MOX, 45 GWd/t	47.0	47.0	5.2	0.8
MOX, 60 GWd/t	46.4	46.4	6.0	12.0

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IV Partitioning and Transmutation Schemes

There are three choices for the management of the spent nuclear fuel from the
world’s 438 commercial nuclear reactors: (a) recycle to recover valuable
components and extract additional energy from the fuel, (b) direct geologic
disposal as waste^{§§§§§§§§§§}, or (c) long-term monitoring after stabilization for
surface or near surface storage. At present, both byproduct recycle and ‘short-
term’ monitoring are being practiced worldwide. After more than 30 years of
continuous investigation, no repositories have been fully licensed to receive
commercial reactor fuels, although Onkalo^{*****} in Finland may be licensed
in the near future. Yet safe disposal of either spent nuclear fuel or the high level
waste (HLW) generated during reprocessing of spent fuel is a matter of great
environmental concern [Baetsle, 1992]. The question of waste disposal has
become the largest single issue standing in the way of further development of
this otherwise environmentally friendly technology. Furthermore, a recent
analysis projecting how fission-based nuclear power could favorably impact
greenhouse gas emissions emphasize the need for breeding additional fuel to

^{§§§§§§§§§§} It is widely accepted the direct geologic disposal of spent fuel requires well-
designed storage for periods ranging in time from tens of thousands to several million
years.

^{*****} The Onkalo (meaning cave or cavity) spent nuclear fuel repository is currently
under construction at the Olkiluoto Nuclear Power Plant in the municipality of Eurajoki
on the west coast of Finland, by the company Posiva.

satisfy the projected long-term uranium shortage. [Hoffert et al., 2002]
Satisfying long-term demand can only be accomplished by closing the loop of the fuel cycle by reprocessing spent nuclear fuel. [Nash 2006]

At present, approximately half of the world's spent nuclear fuel is produced in a 'once through cycle'. The other half is reprocessed to recycle uranium and plutonium to the head-end of the fuel cycle. A deep geological repository is still considered the best option for the sequestration of either spent nuclear fuel or HLW by-products of reprocessing from the environment. Without actinide partitioning and transmutation, radioactivity levels in a repository will remain above natural backgrounds for several hundred thousand to several million years. The objective of transmutation is to change (long-lived) actinides into fission products and long-lived fission products into significantly shorter-lived nuclides. The goal is to have wastes that become radiologically innocuous in only a few hundred years. How to accomplish long term surveillance of a geologic repository to make reliable predictions on the projected lifetime of the engineered and natural barriers beyond a period of 10,000 years (which time exceeds that of all human history) and, above all, public acceptance of such repositories are key questions that impact the future of nuclear power. [Nash 2006, WNA 2015, IAEA 2010]

To obtain public acceptance of future nuclear fuel cycle technology, new and innovative concepts must overcome the present concerns with respect to both environmental compliance and proliferation of fissile materials. [IAEA 2010]
Both concerns can be addressed through partitioning and transmutation of the minor actinides. The Partitioning and Transmutation (P&T) Program is envisioned to separate the fuel into (1) a transuranic (TRU) product stream for conversion to a MOX reactor fuel, (2) separate technetium-99 (^{99}Tc) and iodine-129 (^{129}I) streams, for conversion to targets for transmutation, and (3) a uranium (U) product stream that meets criteria for disposal as a Class C low-level waste (LLW).

A major driver for this program is to save space inside HLW disposal sites, such as the Yucca Mountain National Waste Repository, by removing the uranium, which makes up the vast majority of the mass and volume of used fuel and recycling it as reprocessed uranium.

This (P&T) scheme is expected to reduce both the long-term radio-toxicity and the radiogenic heat production from the HLW waste. (The trivalent Lanthanides {Ln(III)}, account for about one third of the total amount of fission products.)

However, the Actinide(III)/ Lanthanide (III) separation is very difficult because An(III) and Ln(III) ions exhibit similar chemical properties. Mixing these minor actinides with plutonium could further enhance proliferation resistance of the separated plutonium. In addition, this P&T scheme is expected to extend the nuclear fuel resources on earth about 100 times because of the recycle and reuse of fissile actinides. [IAEA 2010, Nash 2006, Madic 2000]

Partitioning approaches can be grouped into aqueous- (hydrometallurgical) and pyrochemical (pyrometallurgical) processes. Most of the partitioning processes studied so far belong to the domain of hydrometallurgy, but, recently, there is a new impetus in the field of pyrometallurgical processes.

A number of aqueous processes based on sequential separation of actinides from spent nuclear fuel have been developed and tested at pilot plant scale; others are at the laboratory scale only. The latest results have been with dry pyro-chemical processes. These processes are mainly in the stage of laboratory studies, very few having been tested on a pilot plant scale. According to the IAEA [IAEA 2010] the scientific objectives of the new approach to research and development are

- To minimize the environmental impact of actinides in the waste stream;
- To develop element-specific, highly durable, materials for solidification and final disposal of residual actinides;
- To develop advanced characterization methods for measurement of actinide hold-up in plants for the purpose of fissile material tracking as needed for nuclear material safeguards and criticality control;
- To establish element specific partitioning criteria to achieve a radio-toxicity reduction of about a factor of 100;
- To define proliferation resistance attributes for the processes and products;
- To compare advantages and disadvantages of aqueous and pyro-partitioning processes; and
- To assess the benefits of partitioning processes by reducing public radiation exposure, decreasing needed final repository capacity, reducing necessity of uranium mining and, consequently, diminishing the impact of uranium mill tailings.

Several factors give rise to a more sophisticated view of reprocessing today, and the use of the term partitioning reflects this evolution in approach.. First, new management methods for high and intermediate-level nuclear wastes are under consideration, notably partitioning-transmutation (P&T) and partitioning and

conditioning (P&C), where the prime objective is to separate long-lived radionuclides from short-lived ones. Secondly, new fuel cycles such as those for fast neutron reactors (including lead-cooled and fused salt reactors), and the possible advent of accelerator-driven systems, require a new approach to reprocessing. Here the focus is on electrolytic processes ('pyroprocessing') in a molten salt bath. The term 'electrometallurgical' is also increasingly used to refer to this processing in the United States.

The main radionuclides targeted for separation for P&T or P&C processing schemes are the actinides neptunium, americium and curium (along with uranium and plutonium) as well as the fission products iodine-129, technetium-99, caesium-135 and strontium-90. Removal of the latter two isotopes significantly reduces the heat load of residual conditioned wastes.

As a result of these views, a number of modifications to the PUREX Process are underdevelopment. These modifications are being attempted for two primary reasons:

1. Nuclear reprocessing reduces the volume of HLW, but does not reduce radioactivity or heat generation and therefore does not eliminate the need for a geological waste repository. The option of partitioning actinides from HLW represents an opportunity to reduce the uncertainties associated with geologic disposal. Partitioning followed by geologic disposal of the trans-plutonium actinides and long-lived fission products can reduce the volume of materials requiring this most expensive form of sequestration, allowing less expensive near surface burial of shorter-lived fission products. Homogeneous feed streams for waste form production (for example, containing only actinides) would enable the use of waste forms specifically designed to accommodate the class of waste being sequestered (as opposed to demanding that one waste form be compatible with the largest part of the periodic table of species present in wastes). The long-term stability of such tailored waste forms would be easier to assure based on analogies with natural systems. An added advantage of this approach is the potential for recovery of the energy value of the actinides. [Nash 2006]
2. Typical plutonium processing today isolates a pure plutonium stream, which is a proliferation concern. Elimination of the isolation of pure plutonium streams would alleviate some of these proliferation concerns.

Efficient separation methods are needed to achieve low residuals of long-lived radionuclides in conditioned wastes and high purities of individual separated

ones for use in transmutation targets or for commercial purposes (*e.g.* ^{241}Am for household smoke detectors). If transmutation targets are not of high purity then the results of transmutation will be uncertain. In particular fertile uranium isotopes (*e.g.* ^{238}U) in a transmutation target with slow neutrons will generate further radiotoxic transuranic isotopes through neutron capture.

Two-step processes are generally considered to be necessary:

- A separation of lanthanides and actinides from fission products in high acidity solutions.
- A separation of actinides from lanthanides from lower acidity solutions.

Achieving effective full separation for any transmutation program is likely to mean electrolytic processing of residuals from the PUREX or similar aqueous processes.

A BNFL-Cogema study in 2001 reported that 99% removal of actinides, ^{99}Tc and ^{129}I would be necessary to justify the effort in reducing the radiological load in a waste repository. A US study identified a goal of 99.9% removal of the actinides and 95% removal of technetium and iodine. In any event, the balance between added cost and societal benefits is the subject of considerable debate.

The process variations reported here should be considered to be typical of on going developments. Any attempt to cover all the possible process variations would be impossible within the space limitations of this chapter. More complete discussions of various flowsheets and processes are more thoroughly discussed elsewhere [IAEA 2010, Nash 2006]. The IAEA documents “Assessment of *Partitioning Processes for Transmutation of Actinides*” [IAEA 2010] and Chapter twenty four, “Actinide Separation Science and Technology” in *“The Chemistry of Actinides & Transactinide Elements”* should be consulted for the details upon which these partitioning processes are based [Nash 2006].

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IV.1 Modifications of the PUREX Process for Partitioning-Transmutation Operations

The aqueous or hydrometallurgical processes developed in the past were seen as an extension of the PUREX Process and separated out the minor actinides (MA) from the HLW by individual processes. This separation would allow the long-term radiotoxic inventories of the packaged waste to be substantially reduced. However, the chemistries of trivalent minor actinides are very similar to trivalent lanthanides, making separation very difficult. The major difference among these methods rests on the nature of the separated product stream. They tend to separate all the actinides together, all the actinides except uranium together, the minor actinides, or the fission products of concern such as iodine, technetium, and cesium. [IAEA 2010, Nash 2006] This problem is being addressed as part of the US Department of Energy’s Fuel Cycle Technology Materials Recovery and Waste Form Development Initiative to address disposal of commercial nuclear reactor fuel and improve the performance of the geologic repository, i.e., it could

be used to save space inside HLW disposal sites, such as the Yucca Mountain Nuclear Waste Repository. [Herczeg 2014, Boyle 2014]

A number of extraction processes have been investigated for use in the partitioning step, the best known is perhaps the TRUEX process based on CMPO, octyl- (phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide and tributyl phosphate (TBP) [Horwitz 1985]. Other partitioning processes such as the DIAMEX process [Moldolo 2007, Cuillerdier 1991, Serrano-Purroy 2005], the TRPO process [Chen 2001], the CTH process [Liljenzin 1984] and the DiDPA process [Kubota 1993] are promising.

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28.4.1.1 Processes for co-extraction of actinides and lanthanides

28.4.1.1 TRUEX⁺⁺⁺⁺⁺ Process

The TRUEX Process was developed at Argonne National Laboratory for removal and recovery of transuranic elements (primarily americium and curium) from certain HLW solutions. [Vandegrift et al . 1984, Horwitz et al. 1985, Leonard 1985, Schulz and Horwitz 1988, Horwitz and Schulz, 1990, IAEA 2010] The process is a multistage solvent extraction system that uses two mixed extractants, octyl(phenyl)-N,N-di-isobutylcarbamoyl-methylphosphine oxide

⁺⁺⁺⁺⁺ TRUEX is an acronym which stands for **TRansUranic **EX**traction**

(CMPO) and tributyl phosphate (TBP), in a diluent that is best selected based on the particular application. The idea is that by lowering the alpha activity of the waste, the majority of the waste can then be disposed with greater ease. The TRUEX Process has been tested with actual HLW) and proved very efficient; it can be used on waste streams to recover lost plutonium and to isolate the americium before converting the remaining waste to a non-transuranic waste. In common with the PUREX Process, this process operates by a solvation mechanism. The TRUEX Process has also been studied in Japan, Russian Federation, Italy and India. [Nash 2006, IAEA 2010, Horwitz 1985, Leonard 1985, Bond 1987, Vandegrift et al . 1984, Horwitz et al. 1985, Schulz and Horwitz 1988, Horwitz and Schulz, 1990, Mathur and Nash 1998, Suresh et al. 2001]

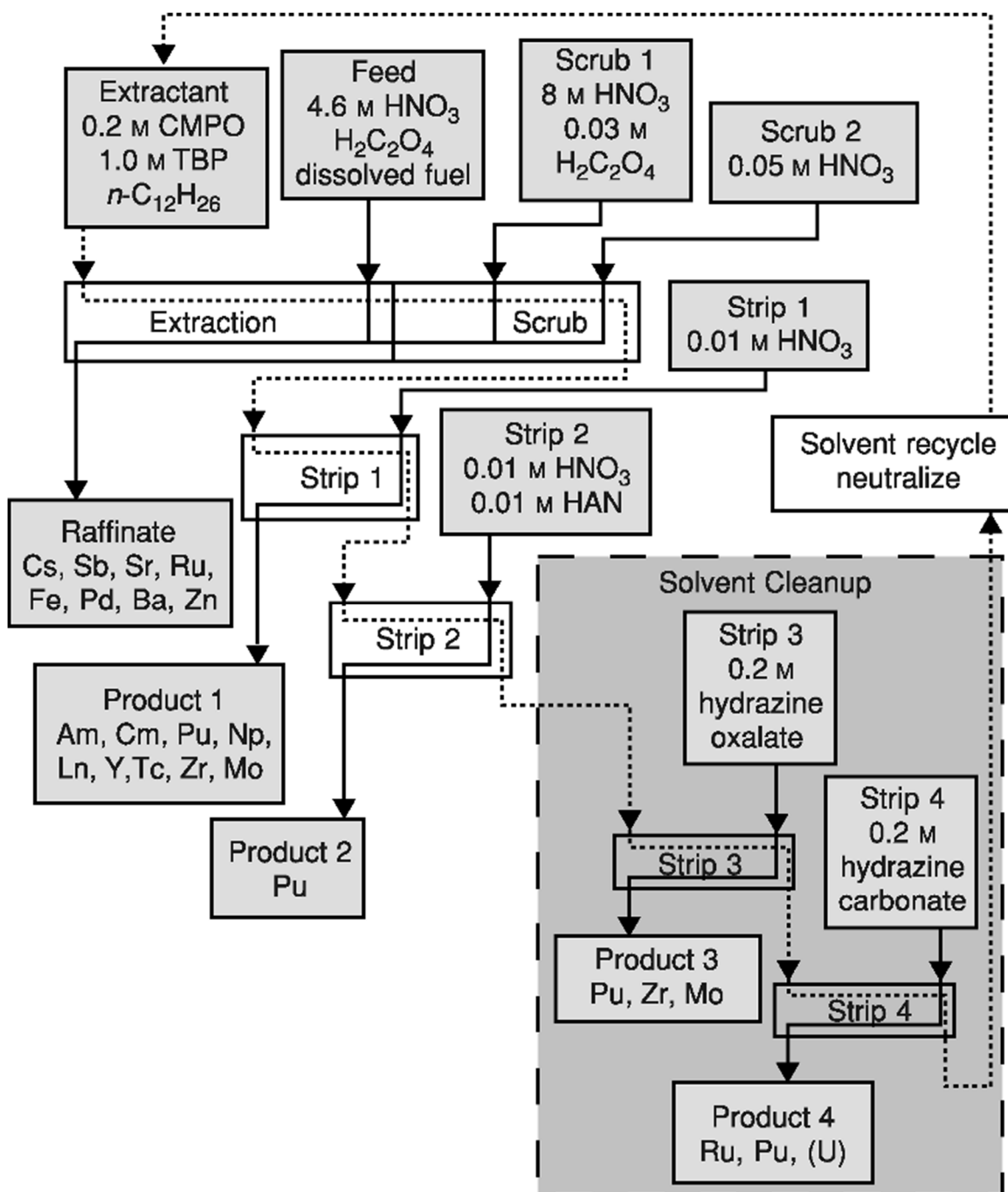


Figure XXX. Generic TRUEX flow sheet for actinide Partitioning at JNC [Nash 2006]

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28.4.1.2 DIAMEX##### Process

As an alternative to the TRUEX Process, an extraction process using a malondiamide has been devised. The DIAMEX Process has the advantage of avoiding the formation of organic waste - the solvent is completely combustible as it contains only the elements carbon, hydrogen, nitrogen, and oxygen. Such an organic waste can be burned without the formation of acidic gases that could contribute to acid rain. Malonamide extractants were proposed initially by Musikas and coworkers in the 1980s and have seen extensive investigation during the intervening years [Musikas, 1987; Cuillerdier et al., 1991a; Nakamura et al., 1995; Nigond et al., 1995; Berthon et al., 1996, 2001; Delavente et al., 1998, 2001, 2003; Erlinger et al., 1998, 1999; Mahajan et al., 1998; Iveson et al., 1999; Madic et al., 2002]. These extractants, functionalized at the alpha-carbon atom with either long chain alkyl groups or alkoxides to improve phase compatibility, compare favorably with CMPO in many respects. The process built around these extractants is referred to as the DIAMEX Process.

DIAMEX is an acronym which stands for **DIAM**ide**EX**traction

The DIAMEX Process is being studied by the European Commission at CEA in France and by the Institute for Transuranium Elements in Germany; the efficiency of the process has been demonstrated by testing with actual HLW in France and other European countries. [IAEA 2010] The French version uses dimethyl-dibutyl-tetradecyl malonamide. The process is sufficiently mature that an industrial plant could be constructed with the existing knowledge of the process. In common with the PUREX Process, this process operates by a solvation mechanism.

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2010

28.4.1.3 TRPO process

As another alternative to the TRUEX Process, an extraction process using phosphine oxide, the TRPO Process, developed in China at the Institute for Nuclear Energy and Technology (Tsinghua University) can remove > 99.9% of the uranium, plutonium, americium, and neptunium from HLW. [Nash 2006, Zhu et al. 1983, IAEA 2010]. Tests were continued in a collaborative effort with the European Institute for Transuranium Elements (Karsruhe, Germany) [Nash 2006, Apostolidis et al., 1991; Zhu and Song, 1992; Glatz et al., 1993, 1995; Song et al., 1994, 1996; Song and Zhu, 1994; Zhu and Jiao, 1994] for the extraction of actinides, lanthanides, and other fission products from HNO₃ and HLW solutions. However, the extractant TRPO extracts U(VI), Pu(IV), Np(IV), and Np(VI) better than Am(III). Also, the TRPO Process has a very complicated partitioning process for the HLW. Some reasonable simplifications for the extraction system will be necessary before a workable process can be demonstrated. [Chen 2001].

A generic flow sheet for partitioning using TRPO is given in Figure XXXX.

TRPO is an acronym that stands for TRialkylPhosphine Oxide Process.

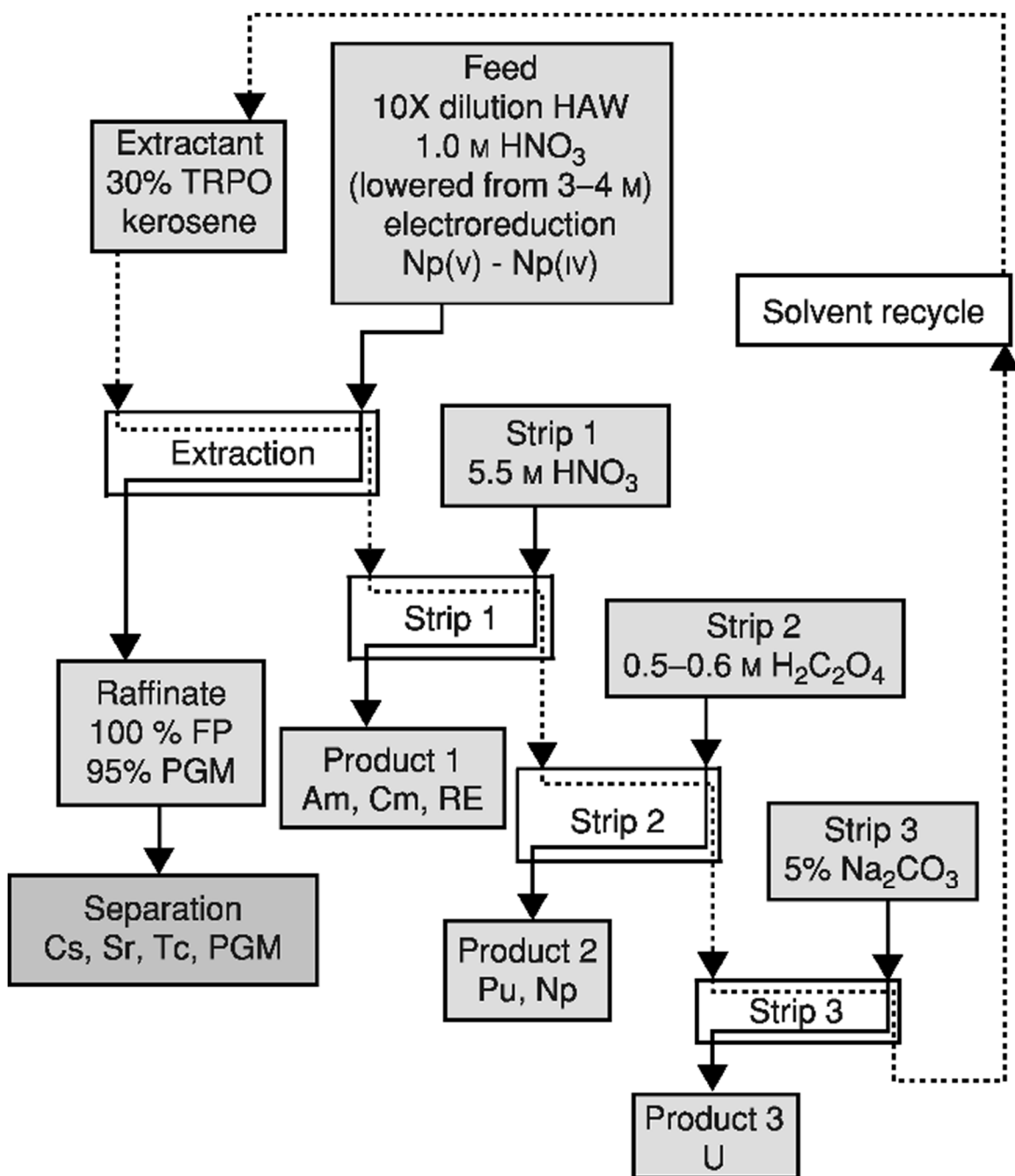


Figure XXXX. Generic flow sheet for actinide partitioning using the TRPO Process. [Nash 2006]

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ARTIST Process

The Japan Atomic Energy Agency (JAEA) has proposed a new chemical process, the ARTIST^{*****} Process, for the treatment of spent nuclear fuel. The main concept is to recover and stock the actinides as two groups: uranium and a mixture of transuranic elements and to dispose solely of fission products. Then the transuranic elements are separated as a group along with lanthanides by using the extractants, TODGA (Tetraoctyl-diglycol-amide) and DHOA (di-n-

***** ARTIST is an acronym that stands for Amide-based Radio-resources Treatment with Interim Storage of Transuranics

hexyl-octanamide). The uranium and the transuranic products are solidified by calcination and are stockpiled for future utilization. Actinides, IAEA-TECDOC-1648, International Atomic Energy Agency, Vienna, 2010

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PROCESSES FOR ACTINIDE-LANTHANIDE SEPARATION

28.4.1.4 TALSPEAK and CTH process

The TALSPEAK Process was developed at the Oak Ridge National Laboratory [Ferguson 1967], in the 1960s, as a possible alternative to the TRAMEX Process. The TALSPEAK Process is an effective method for the separation of americium and curium from the lanthanides. Basically, the TALSPEAK Process provides preferential complexing of the trivalent actinides by an aminopolyacetic acid, so that the lanthanides and yttrium are extracted by a monoacidic organophosphate or phosphonate. The actinides are then extractable with a dilute solution of di(2-ethylhexyl)phosphoric acid (HDEHP) in a suitable hydrocarbon diluent.

As another alternative to TRAMEX, the CTH^{§§§§§§§§§§} process, which was studied in Sweden using D2EHPA {di-2-ethylhexylphosphoric acid} in an aliphatic diluent and TBP in a hydrocarbon diluent. However, a good separation of all the actinide elements cannot be obtained at any single acidity. The three-step procedure:

1. In the first cycle, D2EHPA extracts uranium, plutonium, and neptunium from the aqueous solution containing the dissolved spent nuclear fuel; the aqueous solution is less than 6M HNO_3 .
2. In the second cycle HNO_3 , technetium, palladium and ruthenium are extracted from aqueous phase with TBP.
3. In the third cycle, rare earth and trans-plutonium elements are extracted by D2EHPA from the aqueous phase, which is at 0.1 M HNO_3 .

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+++++++ TALSPEAK is an acronym that stands for Trivalent Actinide Lanthanide Separations by Phosphorus-reagent Extraction from Aqueous Komplexes

TRAMEX is an acronym that stands for **TeRtiary AMine EXtraction**. It was a high-pressure ion exchange process to separate and purify curium and californium at the Savannah River Site.

CTH is an acronym that stands for Chalmers Tekniska Hogskola.

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SANEX Process

The SANEX Process^{*****} is a generic name for one of the four processes, which separates selectively the trivalent actinides (viz., americium and curium) from the lanthanides in the highly acidic waste feeds. These processes could be categorized in two distinct groups based on the chemical nature of the extractant namely:

- i) Acidic sulfur-bearing extractants; and
- ii) Neutral nitrogen-bearing extractants. [IAEA 2010]

Germany has researched a variant of the SANEX Process using an organic phase comprising TODGA⁺⁺⁺⁺⁺ in TPH⁺⁺⁺⁺⁺ + 5% 1-octanol and an aqueous phase containing SO₃-Ph-BTP^{ssssssssss} for the selective strip. This single-cycle SANEX Process is dedicated to recover the minor actinides directly from a PUREX raffinate by selective extraction. [Magnusson 2012, Wilden 2010] The SANEX-BTP Process using Bis-triazinyl-pyridines (BTPs) has been developed at CEA-Marcoule to separate An(III) from Ln(III) ions. [Hill 2002]

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***** SANEX is an acronym that stands for Selective ActiNide EXtraction
 +++++ TODGA is an acronym that stands for the promising tridentate diglycolamide ligand N,N,N',N'-Tetraoctyl Diglycolamide
 +++++ TPH is an acronym standing for hydrogenated tetrapropene
 sssssssssss SO₃-Ph-BTP is shorthand designation for bis-triazinyl-pyridine

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CYANEX 301 process (Acidic Sulfur-bearing extractants)

CYANEX represents compounds, which belong to the family of organo-dithiophosphinates (R₂PSSH, with R = an alkyl group) including CYANEX – 301 (dialkyl 1-dithiophosphinic acid). This process was developed in China in 1995 and uses a mixture consisting mainly of bis (2.4.4. – trimethylpentyl) dithiophosphinic acid. [IAEA 2010] Efficient use of this process requires the feed solution be adjusted to between pH 3 to 5, which is not so easy to carry out industrially.

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ALINA process (Acidic S-bearing extractants)

The ALINA ***** Process was developed in Germany using a synergistic mixture of bis(chlorophenyl)dithio-phosphinic acid ((ClΦ)2PSSH)+++++++ and tri-n-octylphosphine oxide (TOPO). The major advantage of the process is that the concentration of nitric acid in the feed can be increased to as high as 1.5 mol/L to increase the separation efficiency of lanthanides and actinides.

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***** ALINA is an acronym that stands for Actinide - Lanthanide Intergroup separation in Acidic medium.

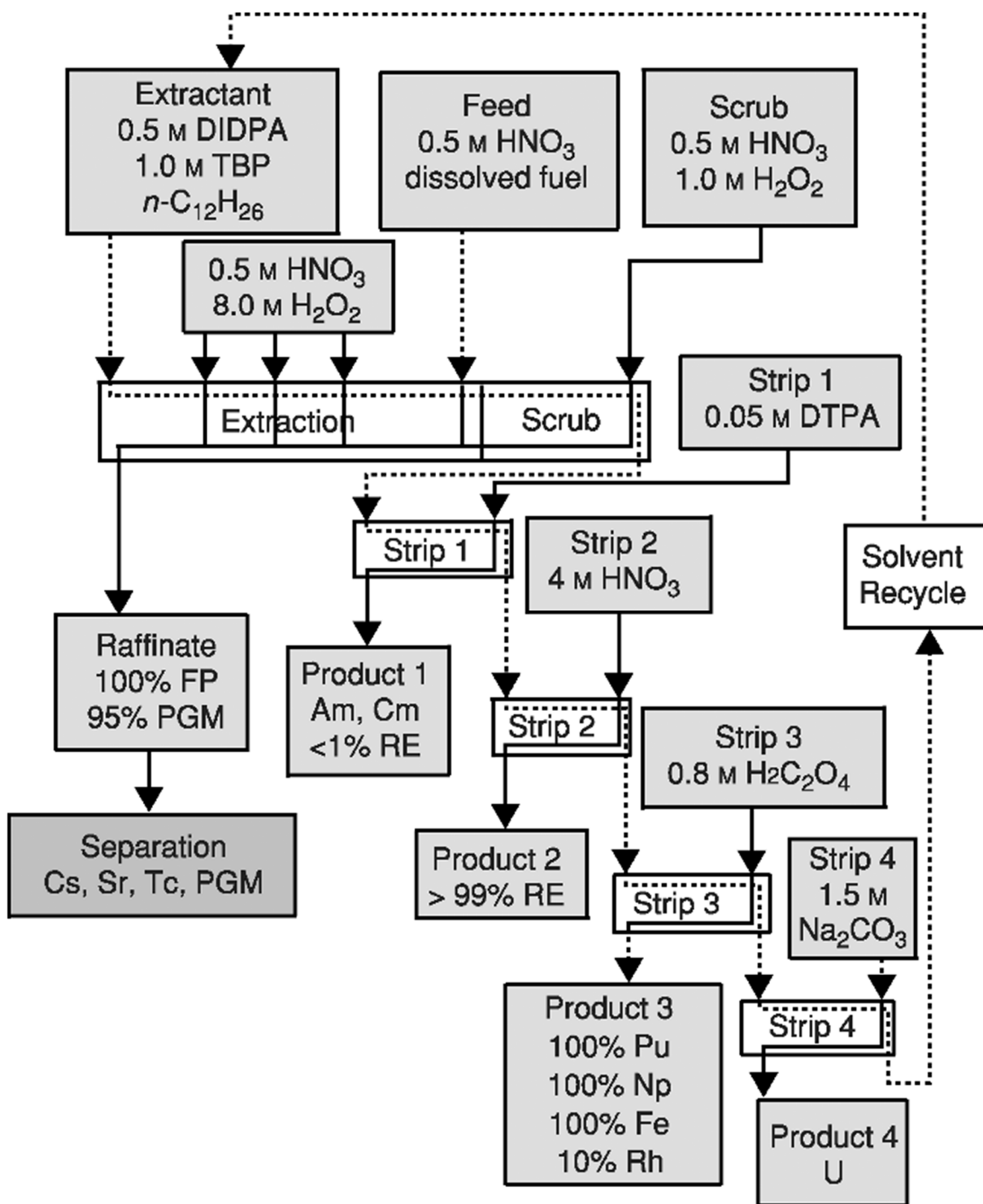
+++++++ ClΦ= chlorophenyl

Processes for Minor Actinide Partitioning

28.4.1.5 DiDPA process

At the Japan Atomic Energy Research Institute, separation of metal ions from the HLW solutions using diisodecylphosphoric acid (DiDPA). The separation of the transuranic elements is done by successive stripping from the loaded solvent, including the use of diethylenetriaminopentaacetic acid (DTPA) complexing agent for An(III)/Ln(III) separation (as is done in TALSPEAK process).

A generic flow sheet for actinide partitioning in the DiDPA process is given in Figure XXXX.



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SEFICS Process

The SEFICS*****Process could be considered as a modified TRUEX process, as it is also based on the same solvent CMPO. It also envisages the use

***** SEFICS is an acronym that stands for Solvent Extraction for Trivalent f-elements Intra-group Separation in CMPO-complexant System

of DTPA for separation of actinides and lanthanides. The process has not been tested with actual HLW materials.

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PALADIN Process

The PALADIN Process is a one-partition cycle process able to separate directly americium and curium from lanthanides and other fission products mixed in concentrated nitric acid (similar to a PUREX raffinate). This process, developed in France, is based on the use of a mixture of extractants: a malonamide (DIAMEX process extractant) plus di-ethylhexylphosphoric acid (HDEHP), and the extractant of the TALSPEAK process.

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PALADIN is the acronym of ‘**P**artition of **A**ctinides and **L**anthanides with **A**cidic extractant, **D**iamide and **I**ncinerable’ complexants.

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28.4.2 Developments of PUREX Modifications to avoid the isolation of pure plutonium streams

A modified version of the PUREX Process that does not involve the isolation of a plutonium stream is the UREX (URanium EXtraction) Process. This process can be supplemented to recover the fission products iodine, by volatilization, and technetium, by electrolysis. Research at the French Atomic Energy Commission (*Commissariat à l'énergie atomique*, CEA) has shown the potential for 95% and 90% recoveries of iodine and technetium respectively. The same research effort has demonstrated separation of cesium. [WNA 2014]

This variation of the PUREX Process was conceived to provide the ability to treat large quantities of spent nuclear fuel and to provide the selectivity required for the process. The PUREX Process was modified so that only uranium, which constitutes the bulk of the mass of spent fuel, and technetium are extracted and the transuranic isotopes are rejected to the aqueous raffinate with the fission products. This URanium EXtraction Process is called UREX. Basically, the UREX Process is the HM Modification of the PUREX Process with a different, more stable reductant.

The demonstration of the UREX Process was performed using a series of 2- cm annular centrifugal contactors installed in shielded cells at the Savannah River National Laboratory.

To prevent the plutonium from being extracted a reductant is introduced before the first metal extraction step. In the UREX process, ~99.9% of the uranium and >95% of technetium are separated from each other and the other fission products and actinides. The key is the addition of acetohydroxamic acid (AHA) to the extraction and scrub sections of the process. The addition of AHA greatly diminishes the extractability of plutonium and neptunium, providing greater proliferation resistance than with the plutonium extraction stage of the PUREX

process.

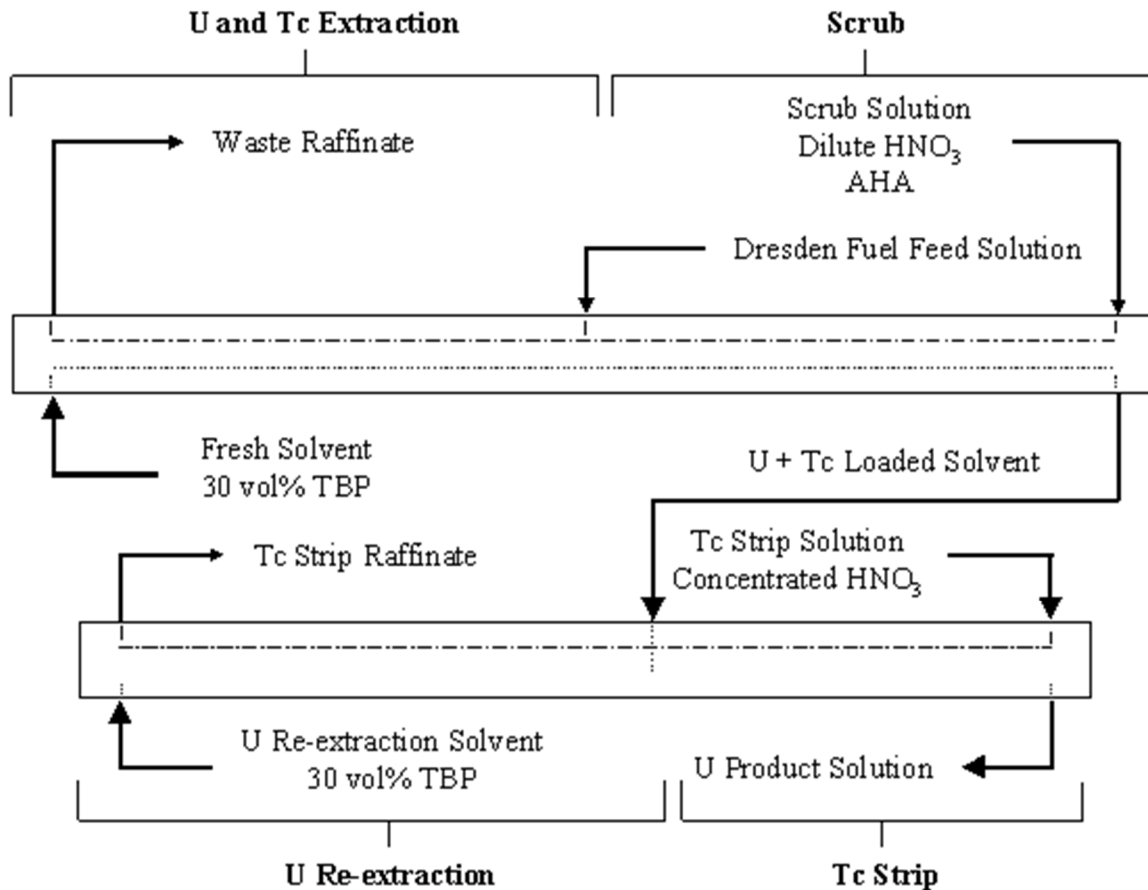


Figure XXXXX Generic flowsheet for UREX process

The US Department of Energy was developing a family of UREX+ Processes under the Global Nuclear Energy Partnership (GNEP) program. In these processes, only uranium and technetium are recovered initially (in the organic phase) for recycle and the residual is treated to recover plutonium with other transuranics. The fission products then comprise most of the HLW. The central feature of this system was to increase proliferation resistance by keeping the plutonium with other transuranics – all of which are then transmuted by recycling in fast reactors.

Several variations of UREX+ Processes have been developed, with the differences being in how the plutonium is combined with various minor actinides, and lanthanide and non-lanthanide fission products are combined or separated. The UREX+1a Process combines plutonium with three minor actinides, but those minor actinides gives rise to problems in fuel fabrication due to americium being volatile and the curium being a neutron emitter. Remote fuel fabrication facilities would therefore be required, leading to high fuel fabrication

costs and requiring significant technological development. An alternative process, the UREX+3 Process, was considered. This process left only neptunium with the plutonium and the result is closer to a conventional MOX fuel. However, the process is less proliferation-resistant than the UREX+1a Process.

Areva and CEA have developed three processes on the basis of extensive French experience with PUREX:

- The COEX ***** Process based on co-extraction and co-precipitation of uranium and plutonium (and usually neptunium) together, as well as a pure uranium stream (eliminating any separation of plutonium on its own). It is close to near-term industrial deployment, and allows high MOX performance for both light water and fast reactors. The COEX Process may have from 20 to 80% uranium in the product; the baseline is 50%.
- The DIAMEX-SANEX [IAEA 2010] Process involves selective separation of long-lived radionuclides (with a focus on americium and curium separation) from short-lived fission products. This process can be implemented with the COEX Process, following separation of uranium/plutonium/neptunium, uranium/plutonium, and minor actinides are recycled separately in Generation IV fast neutron reactors.
- The GANEX+++++++ Process [IAEA 2010] co-precipitates some uranium with the plutonium (as with the COEX Process), but then separates minor actinides and some lanthanides from the short-lived fission products. The uranium, plutonium, and minor actinides together become fuel in Generation IV fast neutron reactors; the lanthanides become waste. It was being demonstrated at ATALANTE+++++++ and La Hague from 2008 as part of a French-Japanese-US Global Actinide Cycle International Demonstration (GACID) with the product transmutation being initially in France's Phoenix fast reactor and subsequently in Japan's Monju fast reactor.

***** COEX is a French process for **CO-EX**tracting uranium and plutonium using extraction methods similar to the PUREX Process.

+++++ GANEX is an acronym that stands for **G**roup **A**cti**N**ides **E**xtraction

ATALANTE is an acronym which stands for **ATelier Alpha et Laboratoires pour ANalyses Tranuraniens et Etudes de retraitement**

- ATALANTE and La Hague from 2008 as part of a French-Japanese-US Global Actinide Cycle International Demonstration (GACID) with the product transmutation being initially in France's Phenix fast reactor and subsequently in Japan's Monju Fast Reactor.

Initial work is at ATALANTE at Marcoule, which started operation in 1992 to consolidate reprocessing and recycling research from three other sites. By 2012, it had demonstrated GANEX, [IAEA 2-10] and fabrication of oxide fuel pins combining U, Pu, Am, Np and Cm. This work will proceed at La Hague on partitioning and fabrication of minor actinide-bearing fuels without the curium. From 2020 these will be irradiated in the Monju Fast reactor, Japan.

All three processes were to be assessed, so that two pilot plants could be built to demonstrate industrial-scale potential:

- One, pilot plant based on the COEX Process, to make the driver fuel for the Generation IV reactor planned to be built by CEA by 2020.
- A second pilot plant would produce fuel assemblies containing minor actinides for testing in Japan's Monju fast reactor and in France's Generation IV fast reactor.

In the longer term, the goal is to have a technology validated for industrial deployment of Generation IV fast reactors about 2040, at which stage the present La Hague plant will be due for replacement.

The U.S. research in recent years has focused on the TALSPEAK Process, which would come after a modified PUREX or COEX Process to separate trivalent lanthanides from trivalent actinides, but this development is only at bench scale so far. Originally in the 1960s it was developed to separate actinides, notably americium and curium from lanthanides.

Another alternative reprocessing technology being developed by Mitsubishi and Japanese R&D establishments is the Super-DIREX (supercritical fluid direct extraction) Process. This process is designed to cope with uranium and MOX fuels from light water and fast reactors. The fuel fragments are dissolved in nitric acid with TBP and supercritical CO₂, which results in uranium, plutonium and minor actinides complexing with TBP.

A new reprocessing technology is part of the reduced-moderation water reactor (RMWR) concept. This technology is the fluoride volatility process, developed

in the 1980s, which is coupled with solvent extraction for plutonium to give Hitachi's Fluorex process. In this, 90-92% of the uranium in the spent nuclear fuel is volatilized as UF_6 , and then purified for enrichment or storage. The residual is put through a PUREX circuit that separates fission products and minor actinides, leaving the unseparated uranium/ plutonium mix (about 4:1) to be made into MOX fuel.

Used MOX fuel can be handled through the PUREX Process, though it contains more plutonium (especially even-numbered isotopes) and minor actinides than used uranium oxide fuel. In 1991-92, 2.1 tonnes of MOX were reprocessed at Marcoule and 4.7 tonnes were reprocessed at La Hague.

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28-4.5 UNEX*****

The UNEX Process was developed in Russia and the Czech Republic; it is designed to completely remove the most troublesome radioisotopes (viz strontium, cesium, and minor actinides) from the raffinate remaining after the extraction of uranium and plutonium from used nuclear fuel. The chemistry is based upon the interaction of cesium and strontium with polyethylene glycol and a cobalt carborane anion (known as chlorinated cobalt dicarbollide). The actinides are extracted by CMPO, and the diluent is a polar aromatic such as nitrobenzene. Other diluents such as *meta*-nitrobenzotrifluoride and phenyl trifluoromethyl sulfone have been suggested as well.

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***** UNEX is an acronym that stand for UNiversal EXtraction

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28.3.4.1 French COEX Process

As an alternative to separating the plutonium as a clean stream, a small amount of recovered uranium can be left with the plutonium, which is to be sent to the MOX fuel fabrication plant; therefore the plutonium is never separated on its own. In France, this is known as the COEX Process. France developed the COEX Process as a “generation III” process; it is not yet in use. In Japan, the new Rokkasho plant uses a modified PUREX Process to achieve a similar result by recombining some of the uranium before the plutonium denitration step; the main product is a 50:50 mixture of uranium and plutonium oxides. [WNA 2015, IAEA 2010]

France is considering the possibility of building a pilot plant to demonstrate the industrial-scale potential of the COEX Process to make the driver fuel for the

Generation IV planned to be built by CEA by 2020. [WNA 2015]

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